OUTLINES OF PHYSICAL CHEMISTRY

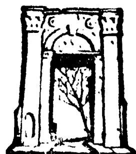
OUTLINES OF PHYSICAL CHEMISTRY

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PREFACE TO FIRST EDITION

THE present book is intended as an elementary introduction to Physical Chemistry. It is assumed that the student taking up the study of this subject has already an elementary knowledge of chemistry and physics, and comparatively little space is devoted to those parts of the subject with which the student is presumed to be familiar from his earlier work.

Physical chemistry is now such an extensive subject that it is impossible even to touch on all its important applications within the limits of a small text-book. I have therefore preferred to deal in considerable detail with those branches of the subject which usually present most difficulty to beginners, such as the modern theory of solutions, the principles of chemical equilibrium, electrical conductivity and electromotive force, and have devoted relatively less space to the relationships between physical properties and chemical composition. The principles employed in the investigation of physical properties from the point of view of chemical composition are illustrated by a few typical examples, so that the student should have little difficulty in understanding the special works on these subjects. Electrochemistry is dealt with

rather more fully than has hitherto been usual in elementary works on Physical Chemistry, and the book is therefore well suited for electrical engineers.

From my experience as a student and as a teacher, I am convinced that one of the best methods of familiarising the student with the principles of a subject is by means of numerical examples. For this reason I have, as far as possible, given numerical illustrations of those laws and formulæ which are likely to present difficulty to the beginner. This is particularly important with regard to certain formulæ—more particularly those in the chapter on Electromotive Force—which cannot easily be proved by simple methods, but which even the elementary student must make use of. The really important thing in this connection is not that the student should be able to prove the formula, but that he should thoroughly understand its meaning and applications.

I have throughout the book used only the most elementary mathematics. In order to make use of some of the formulæ, particularly those in the chapters on Velocity of Reaction and Electromotive Force, an elementary knowledge of logarithms is required, but sufficient for the purpose can be gained by the student, if necessary, from a few hours' study of the chapter on "Logarithms" in any elementary text-book on Algebra.

The experiments described in the sections headed "Practical Illustrations" at the conclusion of the chapters can in most cases be performed with very simple apparatus, and as many as possible should be done by the student. The majority of them are also well adapted for lecture experiments. The more elaborate experiments which are usually performed during a course of practical Physical Chemistry are also mentioned for the

sake of completeness ; for full details a book on Practical Physical Chemistry should be consulted.

In drawing up my lectures, which have developed into the present book, I have been indebted most largely to the text-books of my former teachers, Ostwald and Nernst, more particularly to Ostwald's *Allgemeine Chemie* (2nd Edition, Leipzig, Engelmann) and to Nernst's *Theoretical Chemistry* (4th Edition, London, Macmillan).[1] The following works, among others, have also been consulted : Van't Hoff, *Lectures on Physical Chemistry ;* Arrhenius, *Theories of Chemistry ;* Le Blanc, *Electrochemistry ;* Danneel, *Elektrochemie* (Sammlung Göschen) ; Roozeboom, *Phasenlehre ;* Findlay, *The Phase Rule ;* Mellor, *Chemical Statics and Dynamics ;* Abegg, *Die elektrolytische Dissociationstheorie.* In these books the student will find fuller treatment of the different branches of the subject. References to other sources of information on particular points are given throughout the book.

The importance of a study of original papers can scarcely be overrated, and I have given references to a number of easily accessible papers, both in English and German, some of which should be read even by the beginner. In the summarising chapter on "Theories of Solution" references are given which will enable the more advanced student to put himself abreast of the present state of knowledge in this most interesting subject.

In conclusion, I wish to express my most sincere thanks to Assistant-Professor A. W. Porter, of University College, London, for reading and criticising the sections on osmotic pressure and allied phenomena, and for valuable advice and assistance on many occasions ; also to Dr. H. Sand, of University College, Nottingham, and

[1] The fifth German edition of Nernst's text-book has now appeared.

Dr. A. Slator, of Burton, for criticising the chapters on Electromotive Force and on Velocity of Reaction respectively. Lastly, I wish to acknowledge my indebtedness to my assistant, Mr. T. J. Ward, in the preparation of the diagrams and for reading the proofs.

G. S.

November 1908

PREFACE TO SECOND EDITION

AS less than two years have elapsed since the appearance of the First Edition, only a few slight alterations have been rendered necessary by the progress of the subject in the interval. The opportunity has, however, been taken to revise the text thoroughly; in one or two places the wording has been slightly altered for the sake of greater clearness, and some misprints have been corrected.

A few additions of some importance have also been made. In conformity with the elementary character of the book, the mathematical proofs of the connection between osmotic pressure and the other properties of solutions which can be made use of for molecular weight determinations were omitted from the first edition. The book has, however, been more largely used by advanced students than was anticipated, and at the request of several teachers the proofs in question have now been inserted—as an appendix to Chapter V. The section dealing with the relationship between physical properties and chemical constitution has been rendered more complete by the insertion of brief accounts of absorption spectra and of viscosity.

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I am again indebted to Professor Porter for much kind advice and assistance, and take this opportunity of expressing to him my grateful thanks. I wish also to acknowledge my indebtedness to a number of friends and correspondents, more particularly to Dr. A. Lapworth, F.R.S., Dr. J. C. Philip, Dr. A. E. Dunstan, Dr. W. Maitland and Mr. W. G. Pirie, M.A. for valuable suggestions.

G. S.

December 1910

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DEFINITIONS AND UNITS[1]

In this section the centimetre-gram-second (C.G.S.) system of units is used throughout, length being measured in centimetres (cms.), mass in grams, and time in seconds.

Density is mass per unit volume : unit, gram per c.c. (cubic centimetre).

Specific Volume (1/density) is volume per unit mass : unit, c.c. per gram.

Velocity is rate of change of position : unit, cm. per sec. or cm./sec.

Acceleration is rate of change of velocity : unit, cm. per sec. per sec. or cm./sec.^{2}.

Momentum is mass × velocity : unit, gram-cm. per sec.

Force is mass × acceleration (rate of change of momentum). Unit, the *dyne*, is that force which is required to produce an acceleration of 1 cm. per sec. per sec. in a mass of 1 gram. As a gram-weight, falling freely, obtains an acceleration of 980·6 cm. per sec. (owing to the attraction of the earth) the force represented by the gram-weight = 980·6 dynes at a latitude of 45° and at sea-level.

Energy may be defined as that property of a body which diminishes when work is done by the body ; and its diminution is measured by the amount of work done.

Work Done is force × distance (the work done by a force is measured by the product of the force and the distance through which the point of application moves in the direction of the force). The unit of work (which is also the unit of energy) is the dyne-centimetre or *erg*. The gram-centimetre unit is sometimes used ; 1 gram-centimetre = 980·6 ergs ; also the joule (= 10^7 ergs) is frequently used, especially in electrical work (see below).

Power is rate of doing work, unit, erg per second.

There are six chief forms of energy : (1) mechanical energy, (2) volume energy, (3) electrical energy, (4) heat, (5) chemical energy, (6)

[1] The more important constants made use of in physical chemistry are collected here for convenience of reference.

radiant energy. These forms of energy are mutually convertible, and according to the law of conservation of energy, there is a definite and invariable relationship between the quantity of one kind of energy which disappears and that which results.

The unit of energy, the erg, has already been defined. It is sometimes convenient to express certain forms of energy in special units, heat, for example, in calories; in the following paragraphs the equivalents in ergs of these special units are given.

Volume Energy is often measured in *litre-atmospheres.* When a volume v_1 of a gas expands to the volume v_2 against a *constant* pressure p, say that of the atmosphere, the external work done by the gas (gained) is $p\ (v_2 - v_1)$. The (average) pressure of the atmosphere on unit area (1 sq. cm.) supports a column of mercury 76 cm. high and 1 sq. cm. in cross-section. Hence the pressure on 1 sq. cm. = 76 × 13·596 = 1033·3 grams weight (as the density of mercury is 13·596), or 1033·3 × 980·6 = 1,013,200 dynes. As the work done is the product of the constant pressure and the increase of volume, 1 litre-atmosphere (the work done when the increase in the volume of a certain quantity of a gas is 1 litre or 1000 c.c.) = 1,013,200 × 1000 = 1,013,200,000 ergs.

Electrical Energy is the product of electromotive force and quantity of electricity, and is usually measured in *volt-coulombs* or *joules.* The *practical* unit of quantity of electricity is the *coulomb*; it is that quantity of electricity which under certain conditions liberates 0·001118 grams of silver from a solution of silver nitrate. If a coulomb passes through a conductor in 1 second, the strength of current is 1 *ampere*; the latter is therefore the practical unit of strength of current. The practical unit of resistance is the *ohm*, which is the resistance at 0° offered by a column of mercury 106·3 cm. long and weighing 14·4521 grams. The practical unit of electromotive force is the *volt*; when a current of 1 ampere passes in 1 second through a conductor of resistance 1 ohm, the electromotive force is 1 volt.

The definitions of the C.G.S. units of electromotive force, current strength and resistance are to be found in text-books of physics, and cannot be given here. It can be shown that 1 ohm = 10^9 C.G.S. units and 1 ampere = 1/10 C.G.S. unit; hence, by Ohm's law, 1 volt = 10^8 C.G.S. units. Further, 1 volt-coulomb or 1 joule = $10^8 \times 10^{-1} = 10^7$ C.G.S. units or 10^7 ergs.

Heat Energy is measured in calories. The mean calorie is 1/100 of the amount of heat required to raise 1 gram of water from 0 to 100° and does not differ much from the amount of heat required to raise 1 gram of water from 15° to 16°. 1 calorie = 42,650 gram-centimetres = 41,830,000 ergs (the mechanical equivalent of heat) = 4·183 joules. One joule = 0·2391 calories. There is no special unit for chemical energy; it is usually measured in volt-coulombs or calories.

The value of R, in the general gas equation (p. 34) for a mol of gas = 84,760 gram-centimetres = 83,150,000 ergs = 8·315 joules = 1·985 calories = 0·08205 litre-atmospheres.

USE OF SIGNS IN ELECTROCHEMISTRY

There has always been much confusion in Electrochemistry as to the proper use of positive and negative signs, and even now no general agreement has been reached on the subject. Recently, however, a simple convention has been suggested by the German Electrochemical Society (Bunsen-Gesellschaft) which promises to find general acceptance. *The potential difference has the positive sign if the metal is charged positively with respect to the solution, and negative if the metal is negatively charged, when metal and solution are combined with a comparison electrode to form a cell* (cf. p. 359). In the present book, while this convention is adopted for the potential series of the elements, etc., the potential differences are often given in absolute value and the E.M.F. of combinations illustrated by the graphic method described on pp. 364, 375, 387 and elsewhere. As a result of considerable experience, it has been found that the graphic method is much more useful in avoiding errors of sign than any convention with regard to the use of signs.

MOLECULAR MAGNITUDES

In dealing with molecular magnitudes a system of units, based on the Ångstrom unit as unit of length has been found very convenient:

Unit of length, Å, 1Ångstrom unit = 10^{-10} metres	= 10^{-8} cm.
Unit of area, $Å^2$	= 10^{-16} sq.cm.
Unit of volume $Å^3$	= 10^{-24} c.c.
Unit of mass	= 10^{-24} grams

As already mentioned (p. 25) the Avogadro number is about $0·6 \times 10^{24}$, more accurately, $0·606 \times 10^{24}$. Using this number it can be deduced that the weight of an individual atom or molecule in Ångstrom units is 1·65 times its atomic or molecular weight. Thus the mass of an atom of hydrogen is $1·65 \times 1·0075 = 1·66$ Å.U.

The relation between this system of representing molecular magnitudes and that indicated on p. 321 is as follows:

$$\mu = 10^{-4} \text{ cm.}; \ \mu\mu = 10^{-7} \text{ cm.} \quad \text{Therefore } \mu\mu = 10 \text{ Å.U.}$$

The wave-length of sodium light is about 5890 Å.U.

OUTLINES OF PHYSICAL CHEMISTRY

CHAPTER I

FUNDAMENTAL PRINCIPLES OF CHEMISTRY THE ATOMIC THEORY

Elements and Compounds—Definite chemical substances are divided into the two classes of *elements* and *chemical compounds*. Boyle, and later Lavoisier, defined an element as a substance which had not so far been split up into anything simpler. The substances formed by chemical combination of two or more elements were termed chemical compounds. This definition proved to be a very suitable one, and retained its value even when many of the substances classed as elements by Lavoisier proved to be complex. In course of time it came to be recognized that the substances which resisted further decomposition possessed certain other properties in common, for example, the so-called atomic heat of solid elements proved to be approximately 6·4 (p. 10), and it was found possible to assign even newly-discovered elements with more or less certainty to their appropriate positions in the periodic table of the elements (p. 22). There are, therefore, conclusive reasons, apart from the fact that they have so far resisted decomposition, for regarding elements as of a different order from chemical compounds, and these reasons remain equally valid when full allowance is made for the remarkable discoveries of the last few years in this branch of knowledge.

Until lately no case of the transformation of one element into another was known, but recent work on radium, by Ramsay and Soddy and others, has shown that this element is continuously undergoing a series of transformations, one of the final products

of which is the inactive gas helium. It might at first sight be supposed that the old view of the impossibility of transforming the elements could be maintained, radium being looked upon as a chemical compound of helium with another element, but further consideration shows that this suggestion is not tenable, as radium fits into the periodic table, and, so far as is known, possesses all those other properties which have so far been considered characteristic of elements as distinguished from chemical compounds.

Evidence is gradually accumulating which indicates that the slow disintegration, with final production of other elements, is not confined to radium alone, but is shown more particularly by certain elements of high atomic weight such as uranium and thorium. It is true that the change is spontaneous, as so far there is no known means of initiating it or even of influencing its rate, but further progress in this direction is doubtless only a matter of time. As the phenomenon in question is probably a general one, it seems desirable to retain the term " element " to indicate a substance which has a definite position in the periodic table, and has the other properties usually regarded as characteristic of elements.

From what has been said, it will be evident that it is difficult to define an element in a few words, but in practice there will probably not be much difficulty in drawing the distinction between elements and compounds. Ostwald [1] (1907) defines an element as a substance which only *increases* in weight as the result of a chemical change, and which is stable under any attainable conditions of temperature and pressure, but in this definition the question of radio-active substances is left out of account.

Laws of Chemical Combination—Towards the end of the eighteenth century, Lavoisier established experimentally the law of the conservation of mass, which may be expressed as follows : *When a chemical change occurs, the total weight (or mass) of the reacting substances is equal to the total weight (or mass) of the products.* As the weight is proportional to the mass or quantity of matter, the above law may also be stated in the form that the total quantity of matter in the universe is not altered in

[1] *Prinzipien der Chemie*, Leipzig, 1907, p. 266.

consequence of chemical (or any other) changes. It is, of course, impossible to prove the law with absolute certainty, but the fact that in accurate atomic weight determinations no results in contradiction with it have been obtained shows that it is valid at least within the limits of the unavoidable experimental error.

The enunciation of the law of the conservation of mass by Lavoisier, and the extended use of the balance, facilitated the investigation of the proportions in which elements combine, and soon afterwards the first law of chemical combination was established by the careful experimental investigations of Richter and Proust. This law is usually expressed as follows :—

A definite compound always contains the same elements in the same proportions.

The truth of this law was called in question by the famous French chemist Berthollet. Having observed that chemical processes are greatly influenced by the relative amounts of the reacting substances (p. 162), he contended that when, for example, a chemical compound is formed by the combination of two elements, the proportion of one of the elements in the compound will be the greater the more of that element there is available. This suggestion led to the famous controversy between Berthollet and Proust (1799-1807), which ended in the firm establishment of the law of constant proportions. It is only within the last few years that the strict accuracy of the law of constant composition has been called in question (p. 4).

In certain cases, elements unite in more than one proportion to form definite chemical compounds. Thus Dalton found by analysis that two compounds of carbon and hydrogen—methane and ethylene—contain the elements in the ration 6 : 2 and 6 : 1 by weight respectively ; in other words, for the same amount of carbon, the amounts of hydrogen are in the ratio 2 : 1. Similar simple relations were observed for other compounds, and on this experimental basis Dalton (1808) formulated the Law of Multiple Proportions, as follows :—

When two elements unite in more than one proportion, for a fixed amount of one element there is a simple ratio between the amounts of the other element.

Dalton's experimental results were not of a high order of

accuracy, but the validity of the law was proved by the subsequent investigations of Berzelius, Marignac, and others.

Finally, there is a third comprehensive law of combination, which includes the other two as special cases. It has been found possible to ascribe to each element a definite relative weight, with which it enters into chemical combination. The Law of Combining Proportions, which expresses this conception, is as follows :—

Elements combine in the ratio of their combining weights, or in simple multiples of this ratio.

The combining weights are found by analysis of definite compounds containing the elements in question. When the combining weight of hydrogen is taken as unity, the approximate values for chlorine, oxygen and sulphur are 35·5, 8 and 16 respectively. These numbers also represent the ratios in which the elements *displace* each other in chemical compounds. Water, for example, contains 8 parts by weight of oxygen to 1 of hydrogen, and when the former element is displaced by sulphur (forming hydrogen sulphide) the new compound is found to contain 16 parts by weight of the latter element. 16 parts of sulphur are therefore *equivalent* to 8 parts of oxygen, and the combining weights are therefore often termed *chemical equivalents.* The chemical equivalent of an element is that quantity of it which combines with, or displaces, one part (strictly 1·008 parts) by weight of hydrogen (*cf.* p. 16).

It must be clearly understood that the above generalizations or laws are purely experimental ; they express in a simple form the results of the investigations of many chemists on the combining powers of the elements, and are quite independent of any hypothesis as to the constitution of matter. Until recently the most careful investigations, in the course of atomic weight determinations, failed to show any deviation from the results to be expected according to the laws. The discovery that many chemical elements are mixtures of isotopes (p. 28), the relative proportions of which may vary, leads to the conclusion that the law of constant proportions cannot be strictly accurate, but so far very few exceptions have been found.[1]

[1] F. W. Aston, *Annual Reports of the Chemical Society for 1924*, p. 243.

Atoms and Molecules—The question now arises as to whether a theory can be suggested which allows of a convenient and consistent representation of the laws enunciated above. The atomic theory, first brought forward in its modern form by Dalton (1808), answers these requirements. Following out an idea of the old Greek philosophers, Dalton suggested that matter is not infinitely divisible by any means at our disposal, but is made up of extremely small particles termed *atoms*; the atoms of any one element are identical in all respects and differ, at least in weight, from those of other elements. By the association of atoms of different kinds, chemical compounds are formed. The laws of chemical combination find a simple explanation on the atomic theory. Since a chemical compound is formed by the association of atoms, each of which has a definite weight, it must be of invariable composition. Further, when atoms combine in more than one proportion, for a fixed amount of atoms of one kind the amount of the other must increase in steps, depending on the relative atomic weight—which is the law of multiple proportions. It is here assumed that the ultimate particles of a compound are formed by the association of comparatively few atoms, and this holds in general for inorganic compounds. Finally, the law of combining weights is also seen to be a logical consequence of the atomic theory, the empirically found combining weights, or chemical equivalents, bearing a simple relation to the (relative) weights of the atoms (p. 14).

When Dalton brought forward the atomic theory, the number of facts which it had to account for was comparatively small. As knowledge has progressed, the atomic theory has proved capable of extension to represent the new facts, and its application has led to many important discoveries. At the present day, the great majority of chemists consider that the atomic theory has by no means outgrown its usefulness.

Fact. Generalisation or Natural Law. Hypothesis. Theory[1]—Chemistry, like most other sciences, is based on facts, established by experiment. A few such facts have already been

[1] H. Poincaré, *La Science et l'Hypothèse*, Paris, Flammarion; Ostwald, *Vorlesungen über Naturphilosophie*, Leipzig, 1902; Alexander Smith, *General Inorganic Chemistry*, London, 1906.

mentioned, for example, that certain chemical compounds, which have been investigated with the greatest care, always contain the same elements in the same proportions. A mere collection of facts, however, does not constitute a science. When a certain number of facts have been established, the chemist proceeds to *reason from analogy* as to the behaviour of systems under conditions which have not yet been investigated. For example, Proust showed by careful analyses that there are two well-defined oxides of tin, and that the composition of each is invariable. From the results of these and a few other investigations, he concluded *from analogy* that the composition of all pure chemical compounds is invariable, although of course very few of them had then been investigated from that point of view. To proceed in this way is to *generalise*, and the short statement of the conclusion arrived at is termed a *generalization* or *law*. It will be evident that a law is not in the nature of an absolute certainty; it comprises the facts experimentally established, but also enables us (and herein lies its value) to foretell a great many things which have not been, *but which if necessary could be*, investigated experimentally. The greater the number of cases in which a law has been found to hold, the greater is the confidence in its validity, until finally a law may attain practically the same standing as a statement of fact. We may confidently expect that however greatly our views regarding natural phenomena may change, such generalisations as the law of conservation of mass will remain valid.

Natural laws can be discovered in two ways: (1) by correlating a number of experimental facts, as just indicated; (2) by a speculative method, on the basis of certain *hypotheses* as to the nature of the phenomena in question. The meaning to be attached to the term "hypothesis" is best illustrated by an example. In the previous section we have seen that the laws of chemical combination are accounted for satisfactorily on the view that matter is made up of extremely small, discrete particles, the atoms. Such a mechanical representation, which is more or less inaccessible to experimental proof, is termed a hypothesis. A hypothesis may then be defined as a mental picture of an unknown, or largely unknown, state of affairs, in terms of something which is better known. Thus, the state of affairs in

gases, which is and will remain unknown to us, is represented, according to the kinetic theory, in terms of an enormous number of rapidly moving perfectly elastic particles, and on this basis it is possible, with the help of certain assumptions, to deduce some of the laws which are actually followed by gases (p. 38).

There does not appear to be any fundamental distinction in the use of the terms hypothesis and theory. A theory may be defined as a hypothesis, many of the deductions from which have been confirmed by experiment, and which admits of the convenient representation of a large number of experimental facts.

There is some difference of opinion as to the value of hypotheses and theories for the advancement of science.[1] The majority of scientists, however, appear to consider that the advantages of hypotheses, regarded in the proper light and not as representing the actual state of affairs, are much greater than the disadvantages. Boltzmann,[2] indeed, maintains that "new discoveries are made almost exclusively by means of special mechanical conceptions."

DETERMINATION OF ATOMIC WEIGHTS

General—After the laws of chemical combination had been established, the next problem with which chemists had to deal was the determination of the relative atomic weights of the elements. This might apparently be done by fixing on one element, say hydrogen, as the standard; a compound containing hydrogen and another element may then be analysed, and the amount of the other element combined with one part of hydrogen will be its atomic weight. It is clear, however, that this will be the case only when the binary compound contains one atom of each element, and it was just this difficulty of deciding the relative number of atoms of the two elements present that rendered the decision between a number and one of its multiples or sub-multiples so difficult.

It has already been pointed out that the amount of an element which combines with, or displaces, 1 part by weight of

[1] Ostwald has treated certain branches of chemistry on a system free from hypotheses.

[2] *Gas Theorie*, Leipzig, 1896, p. 4.

hydrogen (strictly speaking, 8 parts by weight of oxygen) is termed the combining weight or chemical equivalent of an element. The first step in determining the atomic weight of an element is to find the chemical equivalent as accurately as possible by analysis and then to find the relation between the atomic weight and chemical equivalent by one of the methods described below. The atomic weight may be equal to, or a simple multiple of, the chemical equivalent.

Dalton, working on the assumption that when two elements unite in only one proportion one atom of each is present, drew up the first table of atomic weights. Water was found by analysis to contain 1 part of hydrogen to 8 parts of oxygen by weight; the atomic weight of oxygen was therefore taken as 8. In the same way, since ammonia contained 1 part of hydrogen to 4·6 parts of nitrogen, the atomic weight of the latter element was taken as 4·6. Great advances in this subject were then made by the Swedish chemist Berzelius. For fixing the proportional numbers, he depended to some extent, like Dalton, on the assumption of simplicity of composition, but was able to check the numbers thus obtained by the application of Gay-Lussac's law of volumes and Dulong and Petit's law. Later still, the discovery of isomorphism by Mitscherlich afforded yet another means of checking the atomic weights. Besides these physical methods, chemical methods may also be used for fixing the atomic weights of the elements. Each of these methods will now be shortly referred to.

(*a*) **Volumetric Method. Gay-Lussac's Law of Volumes. Avogadro's Hypothesis**—Gay-Lussac, on the basis of an extensive series of experiments on the combining volumes of gases, established the law of gaseous volumes, which may be expressed as follows:—

Gases combine in simple ratios by volume, and the volume of the gaseous product bears a simple ratio to the volumes of the reacting gases, when measured under the same conditions.

A few years before, the same chemist had discovered that all gases behave similarly with regard to changes of pressure and temperature, and this fact, taken in conjunction with the law of volumes and the atomic theory, seemed to point to some simple relation between the number of particles in equal volumes

of different gases. Berzelius suggested that equal volumes of different gases under corresponding conditions of temperature and pressure, contain the same number of atoms. It was soon found, however, that this assumption was untenable, and the view held at the present day was first enunciated by the Italian physicist Avogadro. He drew a distinction between *atoms*, the smallest particles which can take part in chemical changes, and *molecules*, the smallest particles which can exist in a free condition, and expressed his hypothesis as follows :—

Equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules.

In expressing the results of determinations of the densities of different gases, hydrogen, as the lightest gas, is taken as standard, and the number expressing the ratio of the weights of equal volumes of another gas (or vapour) and hydrogen, measured under the same conditions, is the density of the gas (or vapour density in the case of a vapour). From Avogadro's hypothesis it follows at once that the ratio of the vapour densities of another gas and hydrogen, being a comparison of the relative weights of an equal number of molecules, is also the ratio of the molecular weights. It is usual to refer both atomic and molecular weights to the *atom* of hydrogen as unity,[1] and therefore the molecular weight, being referred to a standard half that to which the vapour density is referred, is double the vapour density.

When the molecular weight is known, it is a comparatively simple matter to establish the atomic weight. As an example, we may employ the volumetric method to fix the atomic weight of beryllium, a matter of great historical interest. It was found by analysis that beryllium chloride contains 4·55 parts of beryllium to 35·5 parts of chlorine by weight ; in other words, the chemical equivalent of beryllium is 4·55. If beryllium be regarded as a bivalent metal (p. 14), the formula for the chloride will be $BeCl_2$, and its atomic weight $2 \times 4·55 = 9·1$. If, however, it is trivalent, the formula for the chloride must be $BeCl_3$, and, to obtain the ratio for Be : Cl found experimentally, its atomic weight must be $4·55 \times 3 = 13·65$. The vapour density of the chloride was determined by Nilson and Petterson, and from

[1] Strictly speaking, to the atom of oxygen as 16 (p. 16).

the result the molecular weight calculated as 80·1. The molecule of beryllium chloride cannot therefore contain more than $35·5 \times 2 = 71$ parts of chlorine, the formula for the chloride is $BeCl_2$, and the atomic weight of beryllium 9·1.

The determination of atomic weights by the volumetric method thus reduces to *finding the smallest quantity of an element present in a molecule, referred to the atom of hydrogen as unity.* If the molecular weights of a large number of volatile compounds containing a particular element are determined, it is practically certain that at least some of the compounds will contain only one atom of the element in question, and the proportion in which the element is present in these compounds is its atomic weight. In the above example, for instance, it has been assumed that only one atom of beryllium is present in the molecule of beryllium chloride of weight 80·1, and the justification for this assumption is that no compound is known the molecule of which contains less than 9·1 parts of beryllium. It is clear that the numbers thus obtained are maximum values, and the possibility is not excluded that the true values may be fractions of those thus arrived at. The values generally accepted are, however, confirmed by so many independent methods that every confidence can be placed in their trustworthiness.

(*b*) **Dulong and Petit's Law**—In 1818, the French chemists Dulong and Petit enunciated the important law that *for solid elements the product of the specific heat and atomic weight is constant, amounting to about* 6·4. This law is a very striking one when the great differences in the magnitude of the atomic weights are taken into account. Thus, the specific heat of lead—the ratio of the quantity of heat required to raise 1 gram of the metal 1° in temperature to that required to raise the temperature of the same weight of water 1°—is 0·031, and its atomic weight 207, the product being 6·4; whilst for lithium, with a specific heat of 0·9 and an atomic weight of 7, the product is 6·3. Since quantities of the different elements in the proportion of their atomic weights require the same amount of heat to raise the temperature by a definite number of degrees, the law may also be expressed as follows: *The atoms of all elements have the same capacity for heat.*

It is clear that this law can be used to determine the atomic weight of an element when the specific heat is known, the quotient of the constant by the specific heat giving the required value. Dulong and Petit's law was largely used by Berzelius in fixing the values of the atomic weights.

The law of Dulong and Petit is only approximately true, the "constant" varying from about 6·0 to 6·7 at fairly high temperatures (p. 155). This degree of concordance is, of course, quite sufficient for fixing the values of the atomic weights, as it is only necessary for this purpose to choose between a number and a simple multiple or submultiple. Moreover, the specific heat varies with the allotropic form of the element as well as with the temperature, and there is much uncertainty as regards the proper conditions for comparison. Regnault, who made a series of very careful determinations of specific heats, showed that most elements of small atomic weight, more particularly carbon, silicon and boron, have exceptionally small atomic heats. Later, however, it was found that the specific heats of these elements increase rapidly with rise of temperature, and at high temperatures their behaviour is in approximate accordance with Dulong and Petit's law. This is clear from the accompanying table, showing the behaviour of carbon (diamond) and boron :—

Carbon (Diamond).			Boron.		
Temp.	Sp. Heat.	Atomic Heat.	Temp.	Sp. Heat.	Atomic Heat.
10°	0·1128	1·33	27°	0·2382	2·61
206°	0·2733	3·25	126°	0·3069	3·40
600°	0·4408	5·28	177°	0·3378	3·70
1000°	0·4589	5·51	233°	0·3663	4·02

The few elements which show this abnormal behaviour are of low atomic weight, but the converse does not hold, as the atomic heat of lithium is normal.

Some years after the introduction of Dulong and Petit's law, a similar law for *compounds* was enunciated by Neumann. He showed that, for compounds of similar chemical character, the product of specific heat and molecular weight is constant—in

other words, the *molecular heats* of similarly constituted compounds in the solid state are equal. In 1864, Kopp extended Neumann's law by showing that the molecular heat of solid compounds is an *additive* property, being made up of the sum of the atomic heats of the component atoms. It follows that in certain cases atoms have the same capacity for heat before and after entering into chemical combination. For example, the specific heat of calcium chloride is 0·174, the molecular heat is therefore $0{\cdot}174 \times 111 = 19{\cdot}3$, and the atomic heat of each atom 6·4.

This law may be used to estimate the atomic heats of substances which cannot be readily investigated in the solid form. The atomic heat of solid oxygen in combination is about 4·0 and of solid hydrogen 2·3.

(*c*) **Isomorphism**—Mitscherlich observed that the corresponding salts of arsenic acid, H_3AsO_4, and phosphoric acid, H_3PO_4, crystallize with the same number of molecules of water, are identical, or nearly so, in crystalline form, and can be obtained from mixed solutions in crystals containing both salts, so-called *mixed crystals*. On the basis of these and similar observations, Mitscherlich established the Law of Isomorphism, according to which compounds of the same crystalline form are of analogous constitution. Thus, when one element replaces another in a compound without altering the crystalline form, it is assumed that one element has displaced the other atom for atom. The replacing quantities of the different elements are therefore in the ratio of their atomic weights, and if the atomic weight of one of them is known, that of the other can be calculated. This principle was largely used by Berzelius for fixing atomic weights before the establishment of Dulong and Petit's law, and afforded a welcome corroboration of those obtained by the use of the law of volumes. The converse to the law of isomorphism does not hold, as elements may displace one another atom for atom with complete alteration of crystalline form.

The principle of isomorphism is, however, somewhat indefinite, inasmuch as even the most closely related compounds are not completely identical in crystalline form, and it is difficult to decide where the line between similarity and want of similarity is to be drawn. Thus the corresponding angles for the naturally

occurring crystals of the carbonates of calcium, strontium and barium are: Aragonite, 116° 10′; Strontianite, 117° 19′; Witherite, 118° 30′. Tutton,[1] from a careful comparative study of the sulphates and selenates of potassium, rubidium and caesium, has shown that each salt has its own specific interfacial angle, but the differences produced by displacing one metal of the alkali series by another does not exceed 1° of arc, and is usually much less. The three most important characteristics for the establishment of isomorphism are:—

(1) The capacity of forming mixed crystals. The miscibility must be complete, or within fairly wide limits of concentration.

(2) Similarity of crystalline form, which must include at least approximate agreement in the values of the geometrical constants.

(3) The capacity of crystals of one substance to increase in size in a saturated solution of the other.

(*d*) **Determination of Atomic Weights by Chemical Methods**— It is evident from the considerations advanced in the section on the determination of atomic weights by volumetric methods (p. 9) that if the composition of a binary compound containing one or more atoms of an element such as hydrogen or chlorine for each atom of an element of unknown atomic weight has been determined by analysis, and if, further, the relative number of atoms of hydrogen or chlorine present is known, the atomic weight of the other element can at once be calculated. In the case of beryllium chloride, it has been shown that the number of chlorine atoms present can be determined by a physical method (p. 9), but such determinations can sometimes be made by purely chemical methods. As an illustration, we will consider the determination of the atomic weight of oxygen. Analysis shows that water contains approximately 1 part of hydrogen to 8 parts of oxygen by weight. If the molecule of water contains one atom each of hydrogen and oxygen, its formula must be HO and the atomic weight of oxygen will be 8; if, on the other hand, two atoms of hydrogen are present, the formula must be H_2O and the atomic weight of oxygen must be 16 in order to obtain the ratio between the weights of the elements found experimentally. It has been found that by the action

[1] *Science Progress*, 1906, 1, p. 91.

of metallic sodium half the hydrogen in water can be displaced, and as by definition atoms are indivisible, this indicates that the molecule of water contains two (or a multiple of two) atoms of hydrogen. The (probable) formula for water is therefore H_2O and the atomic weight of oxygen 16.

It will be evident that, as in the case of the volumetric method, the value thus obtained for the atomic weight is a maximum and further experiments are necessary to fix the value definitely.

Relation between Atomic Weights and Chemical Equivalents. Valency—The exact proportions in which the elements enter into chemical combination are determined by analysis, and the numbers thus obtained, referred to a definite standard, represent, according to the atomic theory, the atomic weights, or simple multiples or submultiples of the atomic weights, of the respective elements. The choice between several possible numbers is based on the methods discussed in the foregoing paragraphs, more particularly on Avogadro's hypothesis, and the fact that these independent methods give the same values affords strong evidence that the numbers thus obtained are the true ones—a view which obtains still further support from the periodic classification of the elements due to Mendeléeff (1869).

The ordinary chemical formulæ with which the student is familiar are based on the atomic weights thus obtained. For example, the formulæ of a number of compounds containing only hydrogen and one other element are as follows: HCl, H_2O, NH_3, CH_4. It is evident from these formulæ that the power of different elements to combine with hydrogen is very different; whilst one atom of chlorine combines with only one atom of hydrogen, one atom of carbon can become associated with no less than four atoms of hydrogen. The combining capacity of an element for hydrogen or other univalent element is termed the *valency* of an element, chlorine being a univalent and carbon a quadrivalent element. A little consideration of the above formulæ will make clear the relationship between the atomic weight and the chemical equivalent of an element. It is clear that an amount of one element equivalent to its atomic weight may combine with (or displace) 1, 2, 3 or more parts of hydrogen by weight, depending on its valency. Since the

chemical equivalent of an element is that amount of it which can combine with or displace *one* part by weight of hydrogen it follows that

$$\frac{\text{Atomic weight}}{\text{Valency}} = \text{Chemical equivalent.}$$

As has been indicated in the foregoing paragraphs, the atomic weight and the chemical equivalent are often determined more or less independently and the quotient of the two values is the valency. In other cases, however (for example, the volumetric method and the chemical method), the chemical equivalent and the valency are determined, and the product of the two is the atomic weight.

The Values of the Atomic Weights—After the establishment of the law of multiple proportions and the formulation of the atomic theory by Dalton, it became a matter of the utmost importance for chemists to determine the atomic weights of the elements with the greatest possible accuracy. This task was undertaken by Berzelius, who, in the course of about six years (1810-1816), fixed the combining weights of most of the known elements. Since then, the determination of atomic weights has proceeded regularly, but on two occasions a special impulse was given to these investigations. The first occasion was a suggestion by Prout that the atomic weights are exact multiples of that of hydrogen. The idea underlying this assertion was that hydrogen is the primary element, the other elements being formed from it by condensation. The results of Berzelius were incompatible with Prout's hypothesis, but as the atomic weights of certain elements undoubtedly approximated to whole numbers, Stas made a number of atomic weight determinations with a degree of accuracy which has only been improved upon in quite recent times. The results obtained by Stas completely disposed of Prout's hypothesis in its original form (cf. p. 31).

The second event which stimulated atomic weight investigations was the development of the periodic classification of the elements. In certain cases, the order of the elements, arranged according to their atomic weights, did not correspond with their chemical behaviour, and Mendeléeff asserted that in these cases the commonly accepted atomic weights were inaccurate. The

investigations undertaken to test these suggestions afforded striking confirmation of Mendeléeff's views in some cases, but not in others. As regards recent progress in this branch of investigation special mention should be made of the determination of the combining ratios of hydrogen and oxygen by Morley [1] and of the comprehensive and masterly investigations of T. W. Richards and his co-workers.[2]

As the combining weights are relative, it is necessary to fix on a standard to which they may be referred. Dalton took the atomic weight of hydrogen, the lightest element, as unit, but Berzelius, from practical considerations, proposed oxygen as standard, putting its atomic weight = 100. The justification for this procedure is that very few elements form compounds with hydrogen suitable for analysis; the majority of determinations have been made with compounds containing oxygen, and until comparatively recently the ratio of the atomic weights of hydrogen and oxygen was not accurately known. Although the hydrogen standard again came into use after the time of Berzelius, mainly because hydrogen was taken as a standard for other properties, yet in more recent times the oxygen standard has again come most largely into use, the atomic weight of that element being taken as 16·00. The unit to which atomic weights are referred is therefore $\frac{1}{16}$ of the atomic weight of oxygen, and is rather less than the atomic weight of hydrogen.[3] Besides the advantage already mentioned, the atomic weights of more of the elements approximate to whole numbers when the oxygen standard is used, which is a distinct advantage, since round numbers are generally used in calculations.

Chemical equivalents, like atomic weights, should be referred to the oxygen standard, and the chemical equivalent of an element is a number representing that quantity of it which combines with, or displaces, 8 parts by weight of oxygen.

The arguments in favour of the oxygen standard seem conclusive, and as it is very confusing to have two standards in

[1] *Smithsonian Contributions to Knowledge*, 1895.

[2] See, for example, *J. Amer. Chem. Soc.*, 1907, **29**, 808-826.

[3] According to the recent determinations of Morley, Rayleigh and others the atomic weight of oxygen is about 15·88 when hydrogen is taken as unit. It follows that on the oxygen standard, O = 16·00, the atomic weight of hydrogen is about 1·008.

general use, it is very satisfactory that the International Committee on Atomic Weights now use the oxygen standard only.

ATOMIC WEIGHTS (1929)

WHERE the last figure of an atomic weight may be in error by several units it is given as a subscript figure. Where the last figure is given in ordinary type its error probably does not exceed one, or at most two, units.

At. No.	Name.	Symbol.	Atomic Weight.	At. No.	Name.	Symbol.	Atomic Weight.
1	Hydrogen .	H	1·0078	47	Silver . .	Ag	107·880
2	Helium . .	He	4·002$_2$	48	Cadmium .	Cd	112·4$_0$
3	Lithium . .	Li	6·94	49	Indium . .	In	114·8
4	Beryllium .	Be	9·02	50	Tin . . .	Sn	118·70
5	Boron . .	B	10·83	51	Antimony .	Sb	121·76
6	Carbon . .	C	12·003$_6$	52	Tellurium .	Te	127·5
7	Nitrogen .	N	14·008	53	Iodine . .	I	126·93$_2$
8	Oxygen . .	O	16·0000	54	Xenon . .	Xe	130·2
9	Fluorine . .	F	19·00	55	Cæsium . .	Cs	132·8$_1$
10	Neon .	Ne	20·18	56	Barium . .	Ba	137·3$_6$
11	Sodium . .	Na	23·000	57	Lathanum .	La	138·9$_0$
12	Magnesium .	Mg	24·30	58	Cerium . .	Ce	140·2
13	Aluminium .	Al	26·97$_0$	59	Praseodymium	Pr	140·9
14	Silicon . .	Si	28·0$_8$	60	Neodymium .	Nd	144·2$_5$
15	Phosphorus .	P	30·98$_2$	61	Illinium . .	Il	—
16	Sulphur . .	S	32·06$_5$	62	Samarium .	Sm	150·4$_3$
17	Chlorine . .	Cl	35·457	63	Europium .	Eu	152·0
18	Argon . .	A	39·94	64	Gadolinium .	Gd	157·0
19	Potassium .	K	39·10$_5$	65	Terbium . .	Tb	159·2
20	Calcium . .	Ca	40·09	66	Dysprosium .	Dy	162·4$_6$
21	Scandium .	Sc	45·1$_5$	67	Holmium .	Ho	163·5
22	Titanium .	Ti	47·90	68	Erbium . .	Er	167·6
23	Vanadium .	V	50·95	69	Thulium . .	Tm	169·4
24	Chromium .	Cr	52·04	70	Ytterbium .	Yb	173·$_0$
25	Manganese .	Mn	54·95	71	Lutecium .	Lu	175·$_0$
26	Iron . .	Fe	55·84	72	Hafnium . .	Hf	178·6
27	Cobalt . .	Co	58·95	73	Tantalum .	Ta	181·3
28	Nickel . .	Ni	58·69	74	Tungsten .	W	184·1
29	Copper . .	Cu	63·55	75	Rhenium .	Re	—
30	Zinc . .	Zn	65·38	76	Osmium . .	Os	191·$_0$
31	Gallium . .	Ga	69·72	77	Iridium . .	Ir	193·0$_4$
32	Germanium .	Ge	72·60	78	Platinum .	Pt	195·2
33	Arsenic .	As	74·93$_4$	79	Gold . .	Au	197·21
34	Selenium .	Se	79·2	80	Mercury . .	Hg	200·6$_0$
35	Bromine . .	Br	79·91$_5$	81	Thallium . .	Tl	204·$_3$
36	Krypton .	Kr	82·9	82	Lead . .	Pb	207·2$_2$
37	Rubidium .	Rb	85·4$_3$	83	Bismuth . .	Bi	209·0$_0$
38	Strontium .	Sr	87·6$_3$	84	Polonium .	Po	—
39	Yttrium . .	Yt	88·9$_3$	85	—	—	—
40	Zirconium .	Zr	91·2	86	Niton . .	Nt	222
41	Niobium .	Nb	93·3	87	(Emanation)	(Em)	
	(Columbium)	(Cb)			—	—	—
42	Molybdenum .	Mo	96·0	88	Radium . .	Ra	225·9$_5$
43	Masurium .	Ma	—	89	Actinium . .	Ac	—
44	Ruthenium .	Ru	101·6$_5$	90	Thorium . .	Th	232·15
45	Rhodium .	Rh	102·9	91	Protoactinium	Pa	—
46	Palladium .	Pd	106·7	92	Uranium .	U	238·1$_5$

The Periodic System—It was early observed that there are some remarkable relationships between the magnitude of the atomic weights of the elements and their chemical behaviour. The most important observation in this connection is that the differences in the atomic weights of successive members of the same group of elements are approximately 16 or a multiple of that number. Thus for the halogen group, F = 19, Cl = 35·5, Br = 80, I = 127, the differences between each element and its immediate predecessor are 16·5, 44·5 and 47 respectively, the latter two numbers being approximately 3 × 16. Further, for the members of the alkali group, Li = 7, Na = 23, K = 39, Rb = 85·5, Cs = 132·9, the differences are 16, 16, 46·5 and 47·2 respectively.

In 1864, a considerable advance was made by the English chemist Newlands, which is summarized in the law of octaves. He pointed out that when the elements, beginning with lithium, are arranged in the order of ascending atomic weights, there is a gradual variation in properties till the eighth element is reached; this element (sodium) shows a strong resemblance to the first element, lithium, the ninth element, magnesium, is similar in chemical behaviour to beryllium, and so on. The first fourteen elements may therefore be arranged as follows:—

Li=7	Be=9	B=11	C=12	N=14	O=16	F=19
Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35·5

and the elements which show similar chemical behaviour are thus brought into the same vertical row. On these lines, but without any knowledge of the views of Newlands, a complete system for classifying the elements, termed the periodic system was later developed by Mendeléeff. The system is based on the observation that when the elements are arranged in the order of ascending atomic weights, *elements with similar chemical properties recur at regular intervals.*

The accompanying table (p. 19), in which the atomic weights are only approximate, is practically the same as that proposed originally by Mendeléeff. Starting with helium = 4 (which was unknown in Newlands' time) we have the arrangement shown in the first line of the table, in which the properties vary regularly from the first member to fluorine. The next

TABLE OF THE ELEMENTS ARRANGED ACCORDING TO THE PERIODIC SYSTEM.

Group.		0.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Valency.		E_0	$E^{I}Cl$ $E_2{}^{I}O$	$E^{II}Cl_2$ $E^{II}O$	$E^{III}Cl_3$ $E_2{}^{III}O_3$	$E^{IV}H_4$ $E^{IV}O_2$	$E^{III}H_3$ $E_2{}^{V}O_5$	$E^{II}H_2$ $E^{VI}O_3$	E_1H $E_2{}^{VII}O_7$	$E^{VIII}O_4$
1st Short Period		He (2) 4·00	Li (3) 6·94	Be (4) 9·02	B (5) 10·83	C (6) 12·00	N (7) 14·01	O (8) 16·00	F (9) 19·00	
2nd Short Period		Ne (10) 20·18	Na (11) 23·00	Mg (12) 24·30	Al (13) 26·97	Si (14) 28·06	P (15) 30·98	S (16) 32·06	Cl (17) 35·46	
1st Long Period	Even Series	A (18) 39·94	K (19) 39·10	Ca (20) 40·09	Sc (21) 45·1	Ti (22) 47·90	V (23) 50·95	Cr (24) 52·04	Mn (25) 54·95	Fe (26), Co (27), Ni (28). 55·84, 58·95, 58·69
	Odd Series		Cu (29) 63·55	Zn (30) 65·38	Ga (31) 69·72	Ge (32) 72·60	As (33) 74·93	Se (34) 79·2	Br (35) 79·91	
2nd Long Period	Even Series	Kr (36) 82·9	Rb (37) 85·4	Sr (38) 87·6	Yt (39) 88·9	Zr (40) 91·2	Nb (41) 93·3	Mo (42) 96·0	Ma (43)	Ru (44), Rh (45), Pd (46) 101·6, 102·9, 106·7
	Odd Series		Ag (47) 107·88	Cd (48) 112·4	In (49) 114·8	Sn (50) 118·70	Sb (51) 121·76	Te (52) 127·5	I (53) 126·93	
3rd Long Period	Even Series	Xe (54) 130·2	Cs (55) 132·8	Ba (56) 137·4	[Rare Earths La (57) to Yb (71)]*	Hf (72) 178·6	Ta (73) 181·3	W (74) 184·1	Rh (75)	Os (76), Ir (77), Pt (78) 191 193·0 195·2
	Odd Series		Au (79) 197·2	Hg (80) 200·6	Tl (81) 204	Pb (82) 207·2	Bi (83) 209·0	Po (84)	— (85)	
4th Long Period	Even Series	Nt (86) 222	— (87)	Ra (88) 226	Ac (89)	Th (90) 232·2	Pa (91)	Ur (92) 238·1		

The numbers in brackets following the symbols of the elements are the atomic numbers.
The atomic weights are placed below the symbols of the elements.
* No satisfactory method of fitting the rare earth elements into the periodic table has been discovered.

element, neon = 20, is an inactive gas, and is therefore placed below helium, sodium falls into its proper place below lithium, and so on. The first and second periods possess 8 elements each. A third period is started with potassium, but in this case it is necessary to pass over 18 elements before another metal (rubidium), bearing a close resemblance to potassium, is reached. Such a period of 18 elements is termed a *long period* in contrast to the two *short periods* of 8 elements each. The whole table is made up of two short and five long periods, but four of the long periods are incomplete and the last one contains only four elements. Each of the long periods is divided into the even series of elements (in the upper line) and the odd series (in the lower line). There is a close resemblance between the elements in the even series in the same vertical row (*e.g.* potassium, rubidium, caesium), and a similar resemblance among the elements in the odd series (*e.g.* copper, silver, gold), but this does not hold when all the elements in a vertical group are compared (*e.g.* potassium, copper, rubidium, silver). The positions of the elements in the periods are fixed by their chemical relationships with those above them (in the vertical rows), and it is assumed that the blanks indicate the positions of elements which have not yet been discovered. The arrangement of the three intermediate elements in each of the first three long periods presented a certain difficulty, and Mendeléeff put them in a group by themselves, the so-called eighth group (group VIII. in the table).

A study of the elements arranged as above reveals many striking regularities. Thus the valency with regard to hydrogen increases regularly up to the middle of a short period and then falls by steps to unity, whilst the valency for oxygen increases regularly from the beginning to the end of a period. Helium and the elements in the same vertical row do not enter into chemical combination, and may therefore be regarded as having zero valency. The valency relations in the long periods are not quite so regular, being complicated by the fact that most of tne elements have several valencies.

Many of the physical properties of the elements, such as the melting-point, the atomic volume and the density, also vary regularly within each period. For example, the melting-points

in the first series gradually rise from helium to carbon and fall again to fluorine, and similarly the elements of highest melting-point (iron, cobalt, nickel, etc.) occur in the middle of the long periods. Besides this variation of physical properties in the horizontal series, there is a similar, but much less marked, variation in the vertical series; in the case of the alkali metals, for example, there is a gradual fall in the melting-point from lithium to caesium.

Not only the physical properties, but also the chemical properties of the elements vary regularly within the periods. Thus the elements on the extreme left hand of the table are inactive gases, those in the second group decompose water and are strongly electropositive, at the middle of the period they appear to be electrically indifferent (carbon, silicon) and towards the right hand strongly electronegative.

The statements in the last three paragraphs are summarized in the periodic law, due to Mendeléeff, which may be expressed as follows: *The properties of the elements, as well as the properties of their compounds, are periodic functions of the atomic weights.*

The arrangement of the elements according to the periodic system is not in all respects satisfactory. Copper, silver and gold do not fit very well into their positions beside the alkali metals, and it has been suggested that they belong more properly to the eighth group, coming after nickel, palladium and platinum respectively. Further, the atomic weight of argon is greater than that of potassium, but the former element must undoubtedly precede the latter in the periodic table. Again, the chemical behaviour of nickel indicates that it should precede cobalt in the periodic table, whereas its atomic weight is somewhat greater than that of the latter element. The question which has raised most discussion in this connection, however, is the relative position of tellurium and iodine. Although from its chemical relationships the latter element must follow tellurium, yet experiment shows that the atomic weight of tellurium is greater than that of iodine. It is at first natural to suppose that there must have been some mistake in determining the atomic weights, but the recent work of Ladenburg, Puccini,

Köthner, Brereton Baker[1] and others leave practically no room for doubt that the facts are as stated. It is unquestionable that the periodic system is of great value, but the above considerations indicate that it is only a first approximation to a satisfactory system. As shown in the following sections, a fuller understanding of the periodic system has been gained in recent years as a result of different lines of investigation bearing on the structure of the atom.

The periodic system is of use mainly in three ways :—

(*a*) As a system of classification which indicates in a fairly satisfactory way the chemical and physical relationships of the elements.

(*b*) For predicting the existence and properties of elements hitherto undiscovered.

(*c*) For enabling us to fix the correct values of the atomic weights of elements which do not form volatile compounds.

When the periodic system was first brought forward, there were more blanks in the table than there are at the present day, and Mendeléeff not only suggested that the positions of these blanks corresponded with hitherto undiscovered elements, but even foretold the properties of the missing members of the series from the known properties of the elements near them in the periodic table. It is an interesting historical fact that within a few years three of the blanks had been filled by elements—gallium (1875), scandium (1879), germanium (1886)—having in all respects the properties foretold by Mendeléeff.

The use of the periodic system for fixing atomic weights will be readily understood from the foregoing. When the equivalent of the element has been determined, it is usually possible to decide which multiple of it is to be taken, as there will in general be only one position in the table into which the element can be satisfactorily fitted.

The Structure of the Atom. Electrons—Within the last thirty years fundamental advances have been made in our knowledge of the structure of the atom which have thrown an entirely new light on the periodic law. The discovery of Röntgen or X-rays by Röntgen in 1895, the study of electric discharge through

[1] *Trans. Chem. Soc.*, 1907, **91**, 1849.

gases by J. J. Thomson and others since 1895, and the investigation of the phenomena of radioactivity first noticed by Becquerel in 1896, have all contributed to our present conceptions on this subject.

When an electric current at high potential is passed through a gas at very low pressure charged particles are shot off from the cathode. The more important properties of these *cathode rays* are as follows :—

(1) They travel in straight lines normal to the surface of the cathode and cast a shadow of an opaque object placed in their path.

(2) They may be deflected from their normal rectilineal course by electromagnetic and electrostatic fields.

(3) They are negatively charged, as shown, for example, by the fact that they discharge a positively charged electroscope.

(4) They act as nuclei for the condensation of supersaturated vapours, thus producing fogs.

(5) They penetrate thin sheets of metal.

(6) There is no difference in the particles derived from different gases, in particular the ratio of the charge carried, e, to the mass of the particle, m, is always the same.

In view of these facts, J. J. Thomson suggested that these negatively charged particles or *electrons* are formed by the disintegration of atoms and that they are common constituents of all atoms.

The velocity of an electron and also the ratio of the electric charge, e, to the mass, m, can be determined by the simultaneous action of an electromagnetic and an electrostatic field on a fine stream of cathode particles. In this way Thomson was able to show that e/m is constant for all electrons, independent of the nature of the electrodes or of the gas in the discharge tube. The value of e/m is about $1{\cdot}79 \times 10^7$ electromagnetic units. The velocity of the particles was found to vary, according to the potential across the terminals, from about 10^9 to 10^{10} cm. per second—$\frac{1}{30}$ to $\frac{1}{3}$ the velocity of light.

The determination of the charge, e, carried by an electron has formed the subject of a large number of investigations. J. J. Thomson's method was based on the observation of C. T. R. Wilson that information can be gained as to the number of

electrons in a confined space by using them (or rather molecules of gas associated with electrons—gaseous ions) as nuclei for the londensation of water vapour. The total amount of moisture in the cloud was determined by weighing, and the size of each drop, and hence the number of drops, obtained by observing the rate of fall of the drops under the influence of gravity. The total charge carried by the cloud was determined by measuring the current passing when a weak electromotive force was employed. The total charge being known and also the number of electrons the charge carried by an individual electron is known. In making the calculation it is assumed that the number of electrons is the same as the number of drops, which is only approximately true. The results obtained by this method do not differ greatly from the value now accepted for *e*.

The most accurate determinations of the magnitude of *e* are due to Millikan. In his latest experiments droplets of oil (used in order to avoid errors due to evaporation) were introduced into a chamber between two charged plates; the space also contained gaseous ions formed by the action of X-rays on the contained air. A small section of the field was illuminated and the behaviour of individual droplets could be observed in a telescope. By collision with the gaseous ions the droplets acquired electric charges. The descent of the charged droplets under the force of gravity could be counteracted by the electric field between the charged plates. The result of the addition of successive ions to a droplet was recorded by change of speed. It was shown that the velocity of the droplet altered by steps as charges were added or removed and the results form the most definite proof of the discrete or "atomistic" character of electricity. No smaller charge than *e* has been observed, and all charges are integral multiples of *e*. The mean value of *e*, according to Millikan, is $1{\cdot}59 \times 10^{-20}$ electromagnetic units.

The Avogadro Number—Long before experiments on the discharge of electricity through gases had proved the discrete character of electricity, the same conclusion had been reached on other grounds. Thus Helmholtz, in 1881, in the course of a lecture on Faraday's laws (p. 243), pointed out that if electricity is conveyed through the solution by the movement of charged particles, which Faraday termed ions, electricity must

itself consist of discrete units, positive and negative, associated with particles of matter. Further, according to Faraday's second law, the liberation of 1 gram (accurately 1·008 gram) of hydrogen or the gram-equivalent of any other element is attended by the passage of 96,500 coulombs through the solution. According to Avogadro's hypothesis, the number of particles in the gram-equivalent of different univalent elements is the same, and therefore each particle must convey the same quantity of electricity. As the charge conveyed by the gram-equivalent (1·008 gram) of hydrogen is 96,500 coulombs or 9650 electromagnetic units, the charge on an individual atom of hydrogen could be determined if the number of atoms in one gram-equivalent or, what is the same thing, the number of molecules in a gram-molecule of hydrogen or any other gas could be determined.

Various lines of evidence, including calculations based on measurements of the viscosity of gases, and the experiments of Perrin on the rate of settling of finely divided particles in a liquid medium, lead to the conclusion that the number of molecules in a gram-molecule of a gas, the so-called Avogadro number, N, is about 6×10^{23}. Using this value of N, the change on an ion of hydrogen or other univalent ion is

$$\frac{9650}{6 \times 10^{23}} = 1 \cdot 61 \times 10^{-20}$$

electromagnetic units (or $1 \cdot 61 \times 10^{-19}$ coulombs). This figure agrees, within the limits of experimental error, with the charge on an electron, as determined by Millikan and others.

The charge on the hydrogen ion, however, is positive, whereas the electron is the unit, or atom, of negative electricity. It might be supposed that units of positive electricity also exist, but so far positive electricity has not been obtained separate from matter. A positively charged body must therefore be regarded as a body which has lost free negative electricity. A negative ion is an atom or group of atoms associated with one or more electrons; a positive ion is an atom or group which has lost one or more electrons.

When N, the Avogadro number, is known the mass of the hydrogen molecule is obtained by dividing the molecular weight

of hydrogen, 2·016 grams, by N, which may be taken as 6×10^{23}. We thus obtain $3{\cdot}36 \times 10^{-24}$ grams as the weight of the hydrogen molecule.

As shown above, the value of e/m for an electron is about $1{\cdot}79 \times 10^{7}$ electromagnetic units. The ratio e/m for the hydrogen ion, obtained by dividing $1{\cdot}61 \times 10^{-20}$ e.m. units by $1{\cdot}68 \times 10^{-24}$, the weight of a hydrogen atom, is $0{\cdot}97 \times 10^{4}$ e.m. units. The ratio e/m for the electron is therefore about 1845 times greater than for the hydrogen ion, and as e is the same for both, the mass of the electron is only 1/1845 of that of the hydrogen atom. Hence the mass of an electron is

$$\frac{1{\cdot}68 \times 10^{-24}}{1845} = 9{\cdot}1 \times 10^{-28} \text{ grams.}$$

For reasons which cannot be considered here this mass applies only to electrons which are moving slowly with reference to the velocity of light. On certain assumptions the radius of the electron can be calculated—the value obtained is about 2×10^{-13} cm. This is much smaller than the radius of an atom, which is of the order 10^{-8} cms.

Radioactivity—The discovery of X-rays with their remarkable properties led to a search among naturally occurring substances to see if any of them emitted radiations with similar properties to X-rays. Becquerel, and afterwards M. and Mme. Curie, found that compounds of thorium and uranium gave out radiations which penetrated opaque substances and rendered gases conducting, and this led to the isolation of radium and other similar substances very much more active than uranium or thorium. Substances which spontaneously emit these ionizing radiations are said to be radioactive. Each radioactive substance has been proved to be a definite chemical element, the atoms of which are continuously disintegrating, giving out certain rays and forming atoms of smaller weight.

Closer examination of the radiation from radioactive substances showed that three types of rays could be distinguished, known respectively as α, β, and γ rays. All three affect a photographic plate, render gases conducting and render certain materials fluorescent, but in other respects they behave very differently.

The α-rays have little penetrating power, and are only slightly affected by a magnet, the direction of deflection showing that they are positively charged. It is now accepted that α-rays consist of helium atoms which have lost two electrons and therefore have a positive charge of two units.

β-rays have at least 100 times the penetrating power of α-rays. They are readily deflected by a magnet, the direction showing that they are negatively charged. It is generally agreed that the β-rays are negative electrons—actual units of electricity, already known from J. J. Thomson's work on discharge through gases.

γ-rays have a penetrating power much greater than that of β-rays, and their ionizing power is small. They are now known to be pulses in the ether of very short wave-length (about 10^{-9} cms.). X-rays are also wave-motions in the ether, but of greater wave-length than γ-rays.

The Nuclear Atom Theory—From the facts cited above it may be assumed that the atoms of different substances contain one or more electrons, which can be liberated under certain conditions. In a neutral atom, such as that of hydrogen or oxygen, the total negative charge on the electrons must necessarily be balanced by an equivalent positive charge. Rutherford, from experiments on the deflection of α-particles on collision with the atoms of a number of different elements, has drawn the conclusion that the positive charge of the atom is concentrated in a very minute nucleus (from 10^{-12} to 10^{-13} cm. in diameter), the free electrons being situated with regard to the nucleus much as planets with regard to the sun. It follows that almost the entire mass of the atom is concentrated in the nucleus. From the magnitude of the deflection suffered by α-rays in passing through thin sheets of foil, Rutherford showed that the number of positive charges on the nucleus is about half the atomic weight. Earlier experiments on the scattering of X-rays had indicated that the number of scattering centres, the electrons in an atom, was also about half the atomic weight so that evidence from both the positive and negative constituents of the atom supported this connection between the electrical charge and the atomic weight.

The Atomic Number—A notable advance in this subject was

made by Moseley in 1914. When cathode rays in an evacuated tube impinge on a plate of metal or other element (the anti-cathode), Röntgen or X-rays of two definite wave-lengths are obtained, these X-ray spectra being characteristic for each element. Moseley showed that the higher the atomic weight of the material of the anti-cathode the shorter the wave-length (or the greater the frequency) of the characteristic X-rays and, further, for elements of wave-length between aluminium and gold, that the square root of the frequency constitutes an arithmetical progression, the order of increasing frequency being that of the elements arranged in the order of their atomic weights, with certain exceptions. Missing elements in the periodic series correspond with gaps in the series of equal increments of the square root of the frequency. We are thus enabled to arrange the elements in a series from H = 1 to Ur = 92, so that successive elements show a constant difference in the square root of the frequency of their characteristic X-ray vibrations. In this list of atomic numbers at the time of Moseley's discovery there were five gaps, but the element of atomic number 72 has since been discovered (compare periodic table, p. 19). Moseley's law indicates that there must be some characteristic quantity for each atom which changes by equal amounts from atom to atom throughout the whole series of elements. The available evidence shows that this characteristic quantity is the resultant positive charge on the nucleus of the atom. There is evidence that in some cases electrons are present in the nucleus. The quantity which alters by equal amounts from atom to atom is not the total number of positive charges in the nucleus, it is the net or resultant positive charge when allowance is made for the fact that some of the positive charges are neutralized by electrons in the nucleus.

The evidence for this conception of the atomic number is given in the next section.

Radioactivity and Atomic Structure. Isotopes—The conclusions drawn from the work of Moseley and others as to atomic structure receive confirmation from the study of radioactivity. In 1907 Boltwood discovered a new radio-element, which he termed ionium, and later investigation showed it to be identical in chemical behaviour with thorium, so that the

two elements could not be separated by chemical means. The analogy is so far-reaching that even the spectra of the elements are believed to be identical. Many other instances of this remarkable phenomenon are now known. Thus radium, mesothorium I, thorium X, and actinium X are chemically non-separable, as are lead, radium B, thorium B, actinium B, and radium B. These results have within the last few years led to a remarkable law which has thrown a flood of light on the periodic system. Different elements occupying the same place in the periodic table are said to be *isotopic.*

It has already been pointed out that when radioactive disintegration occurs, α-rays (helium atoms with a double positive charge) and β-particles (negative electrons) are expelled. There is evidence that when an atom disintegrates it is the nucleus which is affected. When the nucleus loses an α-particle with its two positive charges the valency of the resulting element will be affected just as in an ordinary electrochemical change of valency. For example, if the element were originally in group IV. of the periodic table, its ion is quadrivalent and carries four unit charges of positive electricity. The expulsion of an α-particle with its two charges brings it into the divalent group II., and the weight of the atom is diminished by four units. On the other hand, the loss of a β-particle, which is a negative electron, increases the positive valency of the product by one. Radium B, for example, isotopic with lead, expels a β-particle and becomes radium C, isotopic with bismuth, the mass being in this case practically unchanged. When one α- and two β-particles are expelled the product occupies the same position in the periodic table as the original element and the two have identical chemical properties, though of different mass.

Another way of stating these rules is that when an α-particle is ejected, the new element occupies a position two spaces to the left in the table or has an atomic number two units lower than that of the parent element. The loss of a β-particle gives an element which occupies the next space to the right in the table, that is the atomic number increases by unity. These two rules can be combined in the statement that *the atomic number changes in the same direction and by the same number of units as the nuclear charge of the atom.* This shows us the true

significance of the atomic number—it is equal to the resultant charge on the positive nucleus of the atom, and therefore also to the number of extra-nuclear electrons in the atom. On this view we may assume that the characteristic radiations are due to systems of electrons which are held in position by the central charge and it is to be expected that the frequency of the vibrations will change by regular increments as the positive charge of the nucleus and therefore also the number of extra-nuclear electrons increases unit by unit.

It follows from the above considerations that the hydrogen atom, with atomic number 1, is made up of a minute nucleus with unit positive charge around which a single electron moves in a circular orbit. It has been shown by Bohr that this conception affords a satisfactory explanation of the hydrogen spectrum.

The helium atom, with atomic number 2, should have a resultant positive charge of 2 units on the nucleus with two extra nuclear electrons. The mass of the helium nucleus is, however, about four times that of hydrogen. The simplest assumption which accounts for the facts is that the helium nucleus consists of four hydrogen atoms or positive nuclei and two electrons, thus giving a resultant charge of 2 and a mass of 4.

So far not much progress has been made in elucidating the structure of more complex atoms.

Modern views of the Periodic Classification—The discovery of isotopes has to a great extent cleared up the difficulties which so long attached to the periodic classification of the elements. We now know that the atomic weight has not the fundamental importance formerly attached to it. The same position in the periodic table may be occupied by a number of elements with the same net nuclear charge and a similar arrangement of the extra nuclear electrons, which accounts for their identical chemical behaviour. They differ only in the weight of the nucleus. The observed atomic weight depends on the respective atomic weights of the different elements and on the relative proportions in which they are present.

The occurrence of isotopes is not confined to radioactive elements. Aston [1] has shown that they occur also among the lighter elements, and further he has reached the remarkable conclusion

[1] *Isotopes* (Edward Arnold, 1922).

that on the basis of oxygen = 16 the atomic weights of the elements, except hydrogen, are whole numbers within the limits of experimental error. Thus chlorine is a mixture of isotopes of atomic weights 35 and 37 and possibly 39, in such proportion as to give the observed atomic weight 35·46. Potassium is a mixture of isotopes of atomic weights 39 and 41, mainly the former, whilst argon consists mainly of an isotope of atomic weight 40 with a small proportion of a second isotope of atomic weight 36. We can therefore easily understand how the observed atomic weight of argon is greater than that of potassium, while the more fundamental property, the respective atomic numbers, are in the order required by their chemical behaviour. The difficulties already alluded to regarding the relative positions of tellurium and iodine and of cobalt and nickel are explained in the same way.

The periodic recurrence of certain properties is plausibly accounted for as being connected with the periodic recurrence of similar arrangements of the extra-nuclear electrons as the atomic number, and therefore the number of extra-nuclear electrons, increases.

The results just described are in full accord with a unitary view of the constitution of matter and, indeed, lend support to Prout's hypothesis that hydrogen is the primary material from which all atoms are built up. Rutherford has proposed the term *proton* for the hydrogen nucleus—the hydrogen atom minus the extra-nuclear electron—and suggests that the helium nucleus is built up of four protons and two electrons, giving the observed resultant positive charge of two. This conception can be extended to other atoms, but so far no very definite evidence is available.

The failure to find a positive electron corresponding in mass with the negative electron has led to the view that the hydrogen nucleus is the positive electron and that matter is built up of positive and negative electrons defined as above.

The deviation of hydrogen from the whole number rule as to atomic weights is accounted for on the view that in the nuclei of normal atoms the packing of the electrons and protons is so close that the additive law of mass does not hold and the mass of the nucleus is less than the sum of the masses of its constituent charges.

CHAPTER II

GASES

The Gas Laws—The gaseous form of matter is characterized by its tendency to fill completely and to a uniform density any available space. In general, gases are less dense than other forms of matter, and their internal friction is much less. In consequence of this, the laws expressing the behaviour of gases under varying conditions are much simpler than those holding for liquids and solids. The most striking fact about these laws is that they are to a great extent independent of the *nature* of the gas: the volume of all gases is affected by changes of temperature and pressure to much the same extent.

The well-known laws which represent more or less accurately the behaviour of *all* gases under varying conditions may be enunciated as follows:—

1. *At constant temperature, the volume, v, of a given mass of any gas is inversely proportional to the pressure, p; otherwise expressed, pv = constant* (Boyle, 1662).

2. *At constant pressure, the volume, v, of a given mass of any gas is proportional to its absolute temperature,* T *(273° + temp. Centigrade)* (Gay-Lussac, 1802).

3. *At constant volume, the pressure of a given mass of any gas is proportional to its absolute temperature.*

These laws are not independent; when any two of them are known, the third can readily be deduced.

The three laws just given may be summarized in a single equation, which represents the behaviour of a gas when any two of the determining factors are varied. Let p_0, v_0 and T_0 represent the original pressure, volume and temperature of a definite quantity of a gas, and p_1, v_1 and T_1 the final values. Suppose that at first the pressure is altered from p_0 to its final value p_1

at constant temperature, then, by Boyle's law, the gas will have a new volume, V, given by the equation $p_0v_0 = p_1V$. Then, keeping the pressure constant at p_1, alter the temperature from T_0 to the final value T_1, the final volume, v_1, will, by Gay-Lussac's law, be given by the equation $V/T_0 = v_1/T_1$. Substituting in the last equation the value of V obtained from the former equation ($V = p_0v_0/p_1$) we obtain

$$\frac{p_0v_0}{T_0} = \frac{p_1v_1}{T_1} = \text{constant}.$$

This may be written in the form $pv = rT$ where r is a constant; in other words, the product of the pressure and volume of a gas is proportional to the absolute temperature.

At a definite temperature and pressure, the volume of the gas, and consequently the value of r, will be proportional to the quantity of gas taken. Further, according to Avogadro's hypothesis, the molecular weight in grams of all gases occupies the same volume under the same conditions. It follows that for these quantities the constant r will have the same value for all gases, quite independent of the conditions under which the gases are measured. This *special* value of the constant may conveniently be represented by R, and we then obtain the equation

$$PV = RT,$$

where V is the volume occupied by the molecular weight of a gas in grams, at the absolute temperature T and under the pressure P—an equation which is of fundamental importance for the behaviour of gases and also for dilute solutions. The molecular weight of a gas in grams, which, according to the atomic theory, represents the weight of the same number of molecules in each case, is conveniently termed a *mol* (Ostwald).

The numerical value of R, in C.G.S. units, may readily be calculated from the accurate observations of the densities of gases made by Regnault, Rayleigh, and others. There is, however, a little uncertainty in the calculation owing to the fact that the volumes occupied by a mol of different gases under equivalent conditions are not quite the same, although very nearly so. Thus 2·016 grams of hydrogen, 32·00 grams of oxygen and

28·02 grams of nitrogen occupy 22·43, 22·39 and 22·40 litres respectively at 0° and 76 cms. Taking 22·40 litres as a mean value, and substituting the values for T (273°) and P ($76 \times 13·59 = 1033·3$ grams per sq. cm.), we obtain

$$R = \frac{PV}{T} = \frac{1033·3 \times 22,400}{273} = 84,760 \text{ gram-cms.} = 83,150,000 \text{ ergs.}$$

As the pressure is measured in gram/cm.^{2}, the volume is of the dimensions cm.^{3}, and T is merely a number, the above value for R is of the form gram × cms. or gram-centimetres. The calorie, the ordinary heat unit, is equal to 42,640 gram-centimetres = 41,830,000 ergs, so that the value of R is almost exactly double (accurately 1·99 times) that of a calorie. We may therefore write the gas equation in the simplified form $PV = 1·99T$, but the approximate form $PV = 2T$ is sufficiently accurate for many purposes. In this form the gas equation is represented in thermal units.

The product PV in the gas equation is of the nature of energy, as is clear from the fact that when a volume, v, of a gas is generated under constant external pressure (say that of the atmosphere) the work done is proportional to the volume and to the pressure overcome, and therefore to their product. The work done by or upon a gas when it changes its volume under a constant external pressure can readily be obtained in thermal units by using the second form of the gas equation given above. Thus if a mol of a gas is generated at 0° under the pressure of the atmosphere, the amount of heat absorbed in performing the external work of expansion, PV, is $2T = 2 \times 273 = 546$ cal.

Since PV is constant, the pressure under which a definite mass of a gas is generated at a definite temperature has no influence on the external work of expansion. Thus, to take the above illustration, if a mol of a gas is generated under a pressure of $\frac{1}{10}$ atmosphere, the volume will be $22·4 \times 10 = 224$ litres, and the work done will again be 546 cal. at 0°.

Deviations from the Gas Laws—Careful experiment shows that although the gas laws, which are summarized in the general formula $PV = RT$, give a general idea of the behaviour of gases, yet they do not represent accurately the behaviour

of any single gas, the deviations depending both on the conditions of observation and on the nature of the gas. It may be said, in general, that the laws are the more nearly obeyed the higher the temperature and the smaller the pressure, and, as regards the nature of the gas, the further it is removed from the temperature of liquefaction. A gas which would follow the gas laws accurately is called a *perfect* or *ideal* gas, and ordinary gases approach more or less nearly to this ideal behaviour.

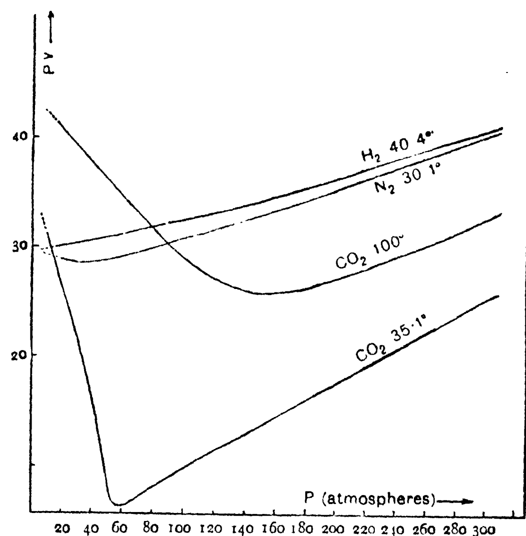


FIG. 1.

The accompanying figure (Fig. 1) gives a graphic representation of the behaviour of the three typical gases, hydrogen, nitrogen, and carbon dioxide, according to Amagat. The product PV, in arbitrary units, is represented on the vertical axis and the pressure P, in atmospheres, along the horizontal axis. If PV were constant (Boyle's law), the curves would be straight lines parallel to the horizontal axis. Actually, PV increases continuously with the pressure in the case of hydrogen, and for nitrogen and carbon dioxide it first decreases, reaches a

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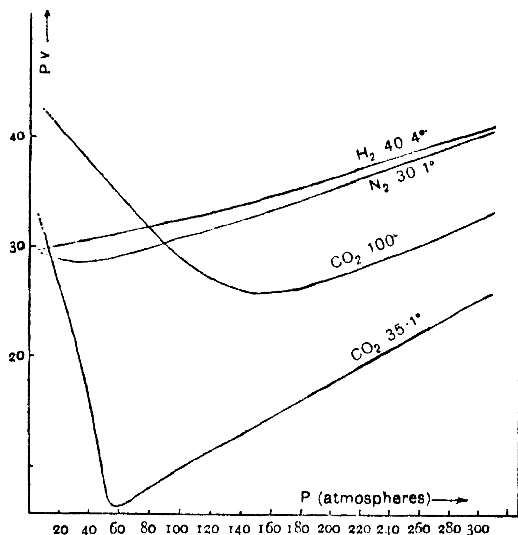


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minimum, and beyond that point increases with increase of pressure. All gases except hydrogen show a minimum in the curve, which indicates that the compressibility is at first greater than corresponds with Boyle's law, reaches a point (which differs for different gases) at which for a short interval Boyle's law is followed, and beyond that point is less compressible than the law indicates. Hydrogen, on the other hand, is always less compressible than the law requires at ordinary temperatures, but at very low temperatures it would also probably show a minimum in the curve. That the deviations from the simple law become less the higher the temperature, is very well illustrated by the curves for carbon dioxide at 35·1° and 100°.

The general behaviour of gases, and the deviations from the simple laws, find a very satisfactory interpretation on the basis of the kinetic theory of gases, which we are now to consider.

KINETIC THEORY OF GASES

General—The fact that the laws followed by gases are so simple in character makes it readily intelligible that attempts to account for their properties on a mechanical basis were made very early in the history of science (Bernoulli, 1738). Our present views on the subject, known as the kinetic theory of gases, are due more particularly to the labours of Clerk Maxwell, Clausius and Boltzmann.

According to the theory, gases are regarded as being made up of small, perfectly elastic particles (the chemical molecules) which are in continual rapid motion, colliding with each other and with the walls of the containing vessel. The space actually *filled* by the gas particles is supposed to be small compared with that which they *inhabit* under ordinary conditions, so that the particles are practically free from each other's influence except during a collision. Owing to the comparatively large free space in which the particles move, an individual particle will move over a certain distance before colliding with another particle; the average value of this distance is termed the "mean free path" of the molecule. On this theory the pressure exerted by the gas on the walls of the containing vessel (which is equal to the pressure under which it is confined) is due to the bombardment

of the walls of the vessel by the moving particles. It is clear that the magnitude of the pressure must depend on the frequency of the collisions, as well as on the mass and velocity of the particles.

Kinetic Equation for Gases—The pressure exerted by a gas can be calculated quantitatively in terms of the number and velocity of the molecules as follows: Imagine a definite mass of a gas contained in a cube, the sides of which are of length l; let n be the number of particles, each of mass m and velocity c. The particles will impinge on the walls in all directions, but the velocity of each may be resolved into three components, x, y, and z, parallel to the edges of the cube, the components being related to the original velocity c by the equation $x^2 + y^2 + z^2 = c^2$. This means that the action on the wall which the molecule would exert if it reached it in the original path with the velocity c is the same as the sum of the effects if the collisions took place successively in directions perpendicular to the three walls at right angles to each other with the velocities x, y, and z respectively. If we consider at first one of the components, the particle will strike the wall at right angles with velocity x, and will fly off with the same velocity in the opposite direction: as the wall and the particle are considered perfectly elastic, there will be no loss of energy in this process. The momentum before the impact is mx, after the impact $-mx$, so that the total change of momentum due to the impact is $2mx$. As the distance between the two parallel walls is l, the particle will perform $\frac{x}{l}$ impacts on the walls in unit time, and as in each of these the change of momentum is $2mx$, the total effect of a single particle in one direction in unit time will be $2mx\frac{x}{l} = 2mx^2/l$. The same applies to the other components of the velocity, so that the total action of a molecule on all six sides of the cube is $\frac{2m}{l}(x^2 + y^2 + z^2) = \frac{2mc^2}{l}$. For the total number of molecules, n, the effect is therefore $2mnc^2/l$. In order to obtain the pressure on unit area, the above value must be divided by the total interior surface of the cube, $6l^2$; we then obtain

$p = \frac{2mnc^2}{6l^3}$, which, since the volume, v, of the cube is l^3, can be put in the more convenient form, $p = \frac{1}{3}mnc^2/v$ or $pv = \frac{1}{3}mnc^2$.

Although the above expression has been deduced only for a cube, it can readily be extended to a vessel of any shape, as follows. The total volume of the latter can be partitioned up into small cubes, and as the pressures on the two sides of the interior walls of these cubes neutralize each other, they do not affect the pressure on the outer walls of the exterior cubes, which in the limit constitute the wall of the containing vessel.

Deduction of Gas Laws from the Equation $pv = \frac{1}{3}mnc^2$—From the above equation, which has been derived on certain more or less plausible assumptions regarding the constitution of gases, some of the laws which have been obtained experimentally may readily be deduced.

Since on the assumptions made in deducing the general formula the right-hand side of the equation is made up of factors which are constant at constant temperature, the product of pressure and volume must also be constant, which is Boyle's law.

Moreover, the above equation may be written in the form $pv = \frac{2}{3} \cdot \frac{1}{2}mnc^2$. As shown in mechanics, the expression $\frac{1}{2}mc^2$ represents the kinetic energy of a particle of mass m and velocity c, and therefore $n \cdot \frac{1}{2}mc^2$ represents the kinetic energy of n particles, so that the product of the pressure and volume of a gas is equal to $\frac{2}{3}$ of the kinetic energy of the molecules. From this it follows that *for equal volumes of different gases under the same pressure, the total kinetic energy of their molecules is the same.*

It has been shown (p. 32) that at constant volume the pressure of a gas varies proportionately with the absolute temperature. In the previous paragraph, it has further been shown that at constant volume the pressure of a gas is proportional to the mean kinetic energy of progressive motion of its particles. Hence *the mean kinetic energy of the molecules of a gas is proportional to its absolute temperature.*[1]

[1] In this case, instead of deducing the experimental law from the kinetic theory, we have made use of the experimental result to obtain a *definition* of temperature on the kinetic theory. *The temperature of a gas is determined by the mean kinetic energy of progressive movement of its molecules.*

Avogadro's hypothesis may now be deduced from the kinetic theory. For equal volumes of two gases at the same pressure we have, from the above equation,

$$pv = \tfrac{1}{3}n_1m_1c_1^2 = \tfrac{1}{3}n_2m_2c_2^2 \quad . \quad . \quad . \quad (1)$$

where n_1 and n_2, m_1 and m_2 and c_1 and c_2 represent the number, mass and velocity of the molecules of the respective gases. Further, if the gases are at the same temperature, the mean kinetic energy of a single molecule is the same for each gas,[1] hence

$$\tfrac{1}{2}m_1c_1^2 = \tfrac{1}{2}m_2c_2^2 \quad . \quad . \quad . \quad . \quad (2)$$

Dividing equation (1) by equation (2) we obtain $n_1 = n_2$, or, otherwise expressed, equal volumes of two gases, under the same conditions of temperature and pressure, contain the same number of molecules, which is Avogadro's hypothesis.

Finally, the mean velocity, c, of the molecules [2] may be calculated by substituting the appropriate values for the other magnitudes in the general equation $pv = \frac{1}{3}mnc^2$. Thus for 1 mol—2·016 grams—of hydrogen under standard conditions, $p = 1033{\cdot}3$ gram/cm.^{2} or $1033{\cdot}3 \times 981$ dynes, $mn = 2{\cdot}016$ grams, $v = 22{,}400$ c.c., we have

$$c_0 = \sqrt{\frac{3pv}{mn}} = \sqrt{\frac{3 \times 1033{\cdot}3 \times 980{\cdot}6 \times 22{,}400}{2{\cdot}016}} = 183{,}900$$

cm. per sec. Therefore the molecule of hydrogen moves at 0° at the enormous speed of 1·839 kilometres or rather more than 1 mile per second. The magnitude of this velocity may seem surprising, in view of the fact that the diffusion of gases, which on the kinetic theory is conditioned by the speed of the molecules, is comparatively slow, but it must be borne in mind that this speed is only attained in the "free path," and owing to collisions and consequent change of path, the actual progress of a particle is very much less. The average speed of the molecules of any other gas may be calculated by substitution in a

[1] This was proved by Clerk Maxwell; it does not follow directly from the above statement.

[2] For a full discussion of the kinetic theory of gases see Jeans, *Dynamical Theory of Gases*, 3rd edition, 1921 (Cambridge University Press).

similar way. It is clear from the form of the equation ($mn/v = d$) that at constant temperature, the rates are inversely proportional to the square root of the densities of the different gases—a result which is connected with the laws of gaseous diffusion (Graham's law) and of gaseous effusion.

Van der Waals' Equation—The kinetic theory of gases not only admits of a simple deduction of the gas laws, but also gives a plausible explanation of the deviation of gases from the simple laws, discussed in the earlier sections. In deducing Boyle's law in the previous section two simplifying assumptions have been made which are not strictly justifiable. In the first place, it has been assumed that in its motion backwards and forwards between the opposite walls of the cube, the molecule has the whole length available for its motion, but a little consideration shows that, if the size of the molecule is not negligible in comparison with this distance, the number of impacts on the walls, and therefore the pressure of the gas, is greater than it would be on the original assumption. To take an extreme case, let us assume that the distance between the walls is 20 times that of the diameter of the molecule, the space available for movement is only 19 molecular diameters, and therefore the pressure will be greater, in the ratio of 20 : 19, than if the size of the molecule could be neglected. This error will clearly be negligible at low pressures (when the total volume is large) but will become important when the gas is strongly compressed. If b is the volume occupied by the molecules, it seems plausible to correct the general gas equation, PV = RT, by substituting for V the total volume occupied by the gas, $v - b$, the "free" volume available for the movement of the molecules, so that the general gas equation becomes $P(V - b) = RT$. In reality, for reasons which cannot be entered into here, b must be taken, not as the volume filled by the material of the molecules, but as a multiple of it, the actual magnitude of which is uncertain.[1]

Another tacit assumption we have made in deducing Boyle's law is that the gas particles exert no mutual attraction, an assumption which is not justified when the gas is strongly com-

[1] According to van der Waals b is 4 times, according to O. E. Meyer $4\sqrt{2}$ times, the actual volume of the molecules.

pressed. A little consideration shows that when increased pressure is applied to a gas, the resulting volume will be less than the calculated value owing to molecular attraction; in other words, the gas behaves as if the pressure applied is greater than it actually is. It was shown by van der Waals that this correction is inversely proportional to the square of the volume, and as, from the above considerations, it affects the gas as an increase of pressure, we must substitute for P, in the gas equation, the expression $P + a/V^2$ where a is a constant. The corrected gas equation then becomes

$$\left(P + \frac{a}{V^2}\right)\left(V - b\right) = RT,$$

an expression, first proposed by van der Waals (1879), which not only represents with fair accuracy the behaviour of strongly compressed gases, but throws considerable light on the constitution of liquids. The detailed consideration of van der Waals' equation is postponed to the next chapter (p. 63) to which it more properly belongs; at present it will be sufficient to show that it affords a satisfactory qualitative explanation of the deviations from the gas laws, discussed on page 35.

When V is very large, b will be negligible in comparison and a/V^2 will be very small, so that van der Waals' equation then approximates to the simple gas equation $PV = RT$. It may therefore be expected that any influence which tends to increase the volume, such as raising the temperature at constant pressure, or diminishing the pressure at constant temperature, will affect the gas in such a way that it follows the simple gas laws more closely, and this expectation is quite borne out by the results of experiment (p. 35). Further, we can employ the equation to explain the fact already referred to, that PV for all gases except hydrogen at first diminishes with increasing pressure, reaches a minimum value, and beyond that point increases steadily as far as the observations extend. From the form of van der Waals' equation it is clear that the volume correction acts in the opposite direction to that for the attraction, the value of PV being increased by the former and diminished by the latter. Increase of PV with increasing pressure means that the gas is

not as compressible as it would be if Boyle's law were obeyed owing to the fact that part of the volume—that represented by b—is practically incompressible; diminution of PV with increasing pressure means that the gas is more compressible than it would be according to Boyle's law, which is ascribed to the effect of attraction. At low pressures the effect of the attraction preponderates, whilst at high pressures the latter is negligible in comparison with the volume correction. At some intermediate pressure (about 50 metres for nitrogen at 30°; see Fig. 1) the two corrections just balance, and in this short region the gas exactly follows Boyle's law.

To explain the behaviour of hydrogen, it is assumed that the attraction correction at ordinary temperatures is from the first counterbalanced by the volume correction.

AVOGADRO'S HYPOTHESIS AND THE MOLECULAR WEIGHT OF GASES

General—As we have already learnt, the application of Avogadro's hypothesis permits of the determination of the molecular weight of any substance which can be obtained in the gaseous form; it is only necessary to find the weight in grams of the substance in question which occupies in the gaseous form a volume of 22·40 litres at 0° and 76 cm. pressure. In determining molecular weights by this method, it is neither necessary nor practicable to work at the temperature or under the pressure referred to; in practice the volume occupied by a known weight of the gas or vapour under suitable and known conditions of temperature and pressure is determined, then with the help of the gas laws the weight in grams which will occupy 22·40 litres under standard conditions is determined. Suppose it is found that g grams of a gas or vapour occupy v c.c. at T° abs. and p millimetres pressure, what weight in grams will occupy 22,400 c.c. at 273° abs. and 760 mm. pressure?

It has already been shown (p. 33) that the expression pv/T is proportional to the mass of the gas, independent of the conditions under which it is measured. It follows that

$$g : \frac{pv}{\mathrm{T}} :: \mathrm{M} : \frac{760 \times 22{,}400}{273}$$

where M is the molecular weight of the gas in grams. Hence

$$M = \frac{g \times 760 \times 22{,}400 \times (273 + t\,°C.)}{273 \times p \times v} \quad . \quad (1)$$

A shorter method is to use the alternative expression for the gas equation[1] $pv = nRT$, where n represents the number of gram-molecules of gas in the volume v. Since $n = g/M$ we have

$$M = \frac{gRT}{pv} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Density and Molecular Weight of Gases and Vapours—The determination of the volume occupied by a known weight of a gas or vapour under definite conditions is equivalent to determining its density, which is the mass per unit volume. The actual determinations may be made in various ways. It will be sufficient for our present purpose to describe Regnault's method, which is particularly suitable for the permanent gases, and the method first suggested by Victor Meyer, which is now used almost exclusively for determining the density, and therefore the molecular weight, of vapours.

(1) *Regnault's Method*—Two glass bulbs of approximately equal capacity and provided with well-ground stop-cocks are used. One is exhausted as completely as possible by means of a pump, weighed, filled at a known temperature and pressure with the gas the density of which has to be determined, and again weighed, the other bulb being used as counterpoise. The volume of the bulb may be obtained by weighing it empty and then filled with distilled water at a known temperature. One of the advantages of using a second bulb is that any risk of error arising from a change in the temperature, pressure or humidity of the air in the balance-case during the weighing is avoided. From the results, the density referred to hydrogen as unity can readily be calculated, and hence the molecular weight, which is double the density (p. 9). The molecular weight can also be obtained by substituting in the formula given above. This method, with slight modifications, has been

[1] Care must be taken to express R in the proper units, corresponding with those in which the pressure and volume are given (*cf.* p. xx).

employed in recent years by Lord Rayleigh, Morley, Ramsay and others for determining the densities of the permanent gases, and is capable of giving results of the highest accuracy.

(2) *Victor Meyer's Method*—This method differs from all the others inasmuch as it is not the volume of the vapour itself which is measured, but that of an equal volume of air which has been displaced by the vapour.

The apparatus consists of a cylindrical vessel, A, of about 200 c.c. capacity, ending in a long neck provided with two side tubes, as shown in Fig. 2. One of these side tubes, t, from which the displaced air issues during an experiment, is bent in such a way that its free end can conveniently be brought under the surface of water in a suitable vessel. Into the other tube, t_2, fits a rubber tube enclosing a glass rod which can be moved outwards and inwards, and, at the commencement of the experiment, serves to retain in place the small glass bulb shown in the figure, containing a weighed quantity of the liquid, the vapour density of which is to be determined. The top of the main tube is closed by a cork which is kept in place throughout an experiment, and a little asbestos or mercury is placed in the bottom to guard against fracture of the glass when the bulb drops. The apparatus is heated at a constant temperature throughout the greater part of its length by means of the vapour of a liquid boiling in the outer bulb-tube, B; the temperature should be at least 20° above the boiling-point of the liquid to be vaporized.

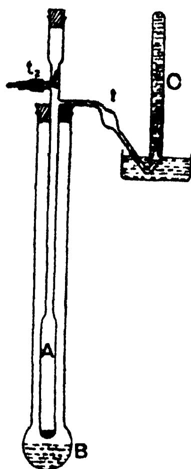


Fig. 2.

At the commencement of an experiment, the bulb and rod are placed in position and the cork inserted, the jacketing liquid is then boiled till air ceases to issue from the end of the tube, t, and bubble through the water, showing that the temperature inside the bulb, A, is constant. A graduated measuring tube, C, full of water, is then inverted over the end of the delivery tube, and the small bulb allowed to drop by drawing back

the glass rod. When air ceases to issue from the end of the delivery tube, the graduated tube is closed by the thumb, removed to a deep vessel containing water, allowed to stand till the temperature is constant, and the volume of air read off when the water outside and inside are at the same level.

The temperature inside the tube, A, is the same before and after the experiment, the only difference in the conditions is that a certain volume of air is displaced by an equal volume of vapour. The observed volume of air is therefore that which the vapour would occupy after reduction to the temperature and pressure at which the air is measured (provided that the vapour and air are equally affected by changes of temperature and pressure, which is approximately the case under suitable conditions). The temperature is that of the water, and the pressure that of the atmosphere less the vapour pressure of water at the temperature of observation. It is clear that it is not necessary to know the temperature at which the substance is vaporized, and this is one of the advantages of the method.

The mode of calculating molecular weights from the observed data may be illustrated by the following example: 0·220 gram of chloroform when vaporized displaced 45·0 c.c. of air, measured at 20° and 755 mm. pressure. As the vapour pressure of water at 20° is 17·4 mm., the actual pressure exerted by the gas is $755 - 17 \cdot 4 = 737 \cdot 6$ mm. Therefore, as 0·220 gram of vapour, at 20° and 737·6 mm. pressure, occupy 45·0 c.c., we have to find what weight in grams will occupy 22,400 c.c., at 273° abs. and 760 mm. pressure, and this will be the required molecular weight. Substituting in the general formula (p. 43) we have

$$M = \frac{0 \cdot 220 \times 760 \times 22{,}400 \times (273 + 20)}{273 \times 737 \cdot 6 \times 45} = 117.$$

This result is in fair agreement with the molecular weight of chloroform (119·5) calculated from its formula.

The results obtained by this method are only accurate if the vapour follows the gas laws as closely as air (since only under these circumstances will the vapour replace an exactly equivalent quantity of air), and as the vapour is often not very remote from its temperature of condensation, this condition is not in

general fulfilled. In the great majority of cases, however, the results are sufficiently near for the purpose, as the composition of the substance can be determined with great accuracy by chemical analysis, and the vapour density method is only used to distinguish between simply related numbers. In the example given above, for instance, analysis shows that the molecular weight of chloroform must be 119·5 or a simple multiple of that number, and the density determination proves that the former alternative is correct.

Results of Vapour Density Determinations. Abnormal Molecular Weights—The most important result of the numerous molecular weight determinations which have been made by this method is that in general the values obtained are in complete agreement with those based on chemical considerations. There are certain exceptions to this rule, but for all these plausible explanations have been suggested. In the case of elements, the values found are simple multiples of the atomic weights (very often twice the atomic weight), whilst in the case of compounds they are simple multiples of the sum of the atomic weights.

All the metals which have been obtained in gaseous form, including mercury, zinc, cadmium, potassium, sodium, antimony, and bismuth,[1] are monatomic, as are the rare elements argon, helium, krypton, etc., discovered in the atmosphere by Ramsay and his co-workers. Many of the non-metals, such as oxygen, nitrogen, and chlorine, are diatomic under ordinary conditions. Whilst arsenic and phosphorus are tetratomic, sulphur at low temperatures gives results corresponding with the formula S_8. Several elements, such as carbon and silicon, and many metals have not yet been obtained in the gaseous form.

The determination of molecular weights at high temperatures has been greatly developed in recent years, more particularly by Victor Meyer and his co-workers, and by Nernst. The air-displacement method has proved most suitable for this purpose, but the chief difficulty has been to obtain vessels which stand high temperatures, and are not porous for the contained vapours. Victor Meyer at first replaced glass by porcelain,

[1] Compare H. von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, **56**, 320; *Abstracts Chem. Society*, 1908, ii., 86.

and the latter by an alloy of platinum and iridium, and at the time of his death was experimenting with vessels of magnesium oxide. Satisfactory results were obtained up to 1700-1800°.

One of the most striking results obtained by Victor Meyer is that the molecular weight of iodine, which at 600° corresponds with the formula I_2, becomes smaller as the temperature is further raised, until at 1500° it reaches half the initial value, indicating that at the latter temperature it is completely split up into iodine atoms. Bromine is also partially decomposed at 1500°, and chlorine commences to split up about the same temperature. It had previously been shown by Deville and Troost that the molecular weight of sulphur also diminishes with increasing temperature, and above 800° gives results which indicate that only diatomic molecules are present.

Nernst[1] has recently succeeded in extending this method up to 2000° by using a vessel of iridium coated outside and inside with a paste of magnesia and magnesium chloride, and heated in an electric furnace. At this temperature, the molecular weight of mercury is 201, indicating that the atoms of this element have undergone no further simplification, whilst sulphur, between 1800° and 2000°, has a density of about 24, indicating that the diatomic molecules are split up, to the extent of about 33 per cent., into single atoms.

Association and Dissociation in Gases—We have already seen that such substances as sulphur and arsenic have abnormally high molecular weights at low temperatures; such substances are said to be *associated*. This pecularity is not confined to elements, as the molecular weight of acetic acid, which, as determined by chemical methods, is 60, exceeds 100 when determined by the vapour density method at comparatively low temperatures. The conclusion that acetic acid in the form of vapour at comparatively low temperatures consists largely of double molecules $(CH_3COOH)_2$, is in satisfactory agreement with other considerations.

An apparent deviation from Avogadro's hypothesis of a different nature is met with, for example, in the case of gaseous ammonium chloride. On chemical grounds, the molecular

[1] Compare Wartenberg, *loc. cit.*

formula, NH_4Cl, is given to this substance, corresponding with a molecular weight of 53·5, whereas the observed value, obtained from its vapour density, is only half as great. This behaviour could be accounted for on the assumption that, at the temperature of the experiment, the molecule is to a great extent split up, or dissociated, into NH_3 and HCl molecules. The experimental justification for this assumption is due to Pebal (1862), who effected a partial separation of the decomposition products by taking advantage of their different rates of diffusion.

It may be added that in the complete absence of moisture, ammonium chloride can be vaporized without dissociation, and then has the normal molecular weight deduced by means of Avogadro's hypothesis.[1]

Accurate Determination of Molecular and Atomic Weights from Gas Densities—We have seen that Avogadro's hypothesis does not hold strictly for actual gases, and that the reason for this is probably to be found in the mutual attractions and finite volumes of the gas particles. We may, therefore, assume that it would be strictly true for an ideal gas, and, on the basis of van der Waals' equation, apply a correction to actual gases to find their true molecular weights, that is, the relative masses which would occupy equal volumes at great rarefaction, when the gas laws would be strictly followed (p. 35). The method followed is therefore to determine the volume of a definite mass of a gas under two or more pressures (the compressibility of the gas), and find by extrapolation the relative densities of different gases as the pressure approaches zero. If a mass W of a gas occupies at 0° a pressure of v litres under a pressure p atmospheres we may call the quotient W/pv the density per unit pressure. If the gas obeyed Boyle's law this would be the same at all pressures, since pv would be constant. If $p = 1$ the quotient $D = W/p_1v_1$ represents the normal density; the limiting value of W/pv as p approaches zero, which we may put as W/p_0v_0, is the limiting density D_0. From these two equations, $D = \frac{W}{p_1v_1}$ and $D_0 = \frac{W}{p_0v_0}$ it

[1] H. Brereton Baker, *Trans. Chem. Society*, 1894, **65**, 611; 1898, **73**, 422 Compare Johnston, *Zeitsch. physikal. Chem.*, 1908, **61**, 457.

follows that limiting density = normal density $\times \frac{p_1v_1}{p_0v_0}$. As already indicated, p_0v_0 is found by making a number of measurements of pv at different values of p, plotting pv against p and extrapolating to $p = 0$. We then apply the principle that the ratio of the limiting densities of two gases is the ratio of their molecular weights.

For gases such as hydrogen and oxygen, which follow the gas laws closely, the correction to be applied to obtain the limiting density from the normal density is small. The data are as follows :—

Hydrogen : normal density, 0·08987 ; limiting density, 0·08992.
Oxygen : ,, ,, 1·42906 ; ,, ,, 1·42768.

The method of determining atomic and molecular weights just described has been used more particularly by Daniel Berthelot and by Lord Rayleigh. From the results, the following molecular weights (vapour density × 2) were calculated by Berthelot (oxygen = 32 being taken as the standard) :—

H_2	N_2	CO	O_2	CO_2	N_2O	HCl
2·0145	28·013	28·007	32·000	44·000	44·000	36·486

From these observations, the following atomic weights have been obtained, the values derived by chemical methods being placed below for comparison :—

	O	H	C	N	Cl
Gas density	16·000	1·0075	12·000	14·005	35·479
Chemical	16·000	1·008	12·00	14·01	35·457

The agreement, except in the case of chlorine, is excellent. As a matter of fact, the density value for chlorine is probably too high; the investigations of Leduc and Briner[1] appear to show that the true value is 35·453, almost identical with that obtained by the chemical method.

The above striking results lend strong support to the assumption that in the limit Avogadro's hypothesis is strictly valid for all gases.

[1] E. Briner, *J. Chim. Phys.*, 1906, 4, 476.

SPECIFIC HEAT OF GASES

General—The specific heat of any substance may be defined as the ratio of the amounts of heat required to raise 1 gram of the substance in question and 1 gram of water through a given range of temperature. The amount of heat required to raise 1 gram of water 1° in temperature is termed a calorie, and hence the specific heat may also be defined as the quantity of heat in calories required to raise 1 gram of the substance 1° in temperature. This statement has only a definite meaning, however, when the conditions under which the heating is carried out are stated, and this is particularly true of gases. If a gas is suddenly compressed it becomes warmer, although no heat has been supplied to it, and, conversely, if a gas is allowed to expand against pressure it becomes cooled, although no heat has been abstracted from it. According to the above definition,

$$\text{Specific heat} = \frac{\text{amount of heat supplied}}{\text{rise in temperature}}$$

so that if a gas is warmed by compression its specific heat is zero. Moreover, if, while a gas is expanding against pressure, sufficient heat is supplied to keep its temperature constant, the heat supplied has a certain finite value whilst the change of temperature is zero, so that the specific heat, according to definition, is infinite. It is clear that the specific heat of a gas may have any value whatever, unless the conditions under which it is measured are stated.

Specific Heat at Constant Pressure, C_p, and Constant Volume, C_v—There are two important cases in which the term "specific heat of a gas" is clearly defined: (*a*) the specific heat at constant volume, C_v, (*b*) the specific heat at constant pressure, C_p. In the former case, the volume is kept constant whilst the gas is being heated, and no external work is done. In the latter case, the volume is allowed to increase whilst heat is being supplied, work is therefore done against the pressure of the atmosphere, which tends to cool the gas. Sufficient heat must therefore be supplied not only to raise the temperature, but to make up for the cooling due to the external work performed. It is clear that the specific heat at constant pressure is greater

than that at constant volume, and the difference is the heat equivalent of the amount of work done against the external pressure.

The difference between the two specific heats may readily be obtained in thermal units by using the general gas equation. For this purpose, it is convenient to deal with a mol of a gas. It has already been shown (p. 34) that when a gas expands at constant pressure, the work done is measured by the product of the pressure and the change of volume. If at first the absolute temperature is T_1, we have the equation $PV_1 = RT_1$ where V_1 is the molecular volume. If the temperature is raised to T_2, and the new molecular volume is V_2, the work done during the expansion is

$$P(V_2 - V_1) = R(T_2 - T_1).$$

In the present case, $T_2 - T_1$ is 1°, therefore $P(V_2 - V_1) = R$. Further, the difference in the molecular heats of a gas at constant pressure and constant volume is the external work done when a mol of gas is raised 1° in temperature, and therefore $M(C_p - C_v)$ (where M is the molecular weight of the gas) is also $= P(V_2 - V_1)$. Hence $M(C_p - C_v) = R$. In thermal units, R is approximately 2 calories, so that the difference of the specific heats of a mol of any gas—in other words, the difference of the molecular heats of any gas at constant pressure and at constant volume—is 2 calories.

The specific heat of a gas at constant pressure can readily be determined by passing a known quantity of it, heated to a definite temperature, through a metallic worm in a calorimeter, at such a rate that there is a constant difference of temperature between the entering and issuing gas. It is more difficult to determine directly the specific heat at constant volume, and this has only been accomplished satisfactorily in comparatively recent times[1] (p. 154).

The molecular heats MC_v and MC_p (molecular weight × specific heat) of a few of the commoner gases at 100° are given in the accompanying table, the values of C_v being obtained from those of C_p by subtracting 2 calories :—

[1] Joly, *Proc. Roy. Soc.*, 1889, 47, 218. Compare Preston, *Theory of Heat*, p. 239.

Gas.	Specific Heat, C_p.	MC_p.	MC_v.	C_p/C_v.
Argon	—	4·98	2·98	1·66
Helium	—	—	—	1·66
Mercury	—	—	2·965	1·66
Hydrogen	3·409	6·880	4·880	1·412
Oxygen	0·2175	6·960	4·960	1·40
Hydrogen chloride	0·1876	6·84	4·84	1·409
Chlorine	0·110	7·80	5·80	1·34
Nitrous oxide	0·2262	9·99	7·99	1·247
Ether	0·4797	35·51	33·51	1·060

For diatomic molecules, the average value of the molecular heat at constant volume is about 4·9 calories in the neighbourhood of 100°; but chlorine and bromine are exceptions. For triatomic molecules the average value of MC_v is 7·5 cal. and the value increases with the complexity of the compound, as is illustrated in the table.

Specific Heat of Gases and the Kinetic Theory—Much light is thrown on the question of the specific heat of gases by the kinetic theory. According to this theory the energy-content of a gas is made up of three parts: (1) energy of translation (rectilineal motion of the molecules), often termed simply kinetic energy (p. 38); (2) energy of vibration of the atoms within the molecule, which is partly kinetic and partly potential; (3) energy of rotation;[1] and when heat is supplied to a gas at constant volume all three factors of the energy may be affected. For monatomic gases, however, such as mercury vapour, the factors (2) and (3) are presumably absent, and the heat supplied must simply be employed in increasing the kinetic energy of the molecules. We have already learnt (p. 38) that the kinetic energy of 1 mol of any gas $= \frac{3}{2}PV = 3T$ if expressed in thermal units. When a gas is raised at constant volume from the absolute temperature T_1 to T_2 we have for the kinetic energies at the two temperatures the equations $\frac{3}{2}P_1V = 3T_1$ and $\frac{3}{2}P_2V = 3T_2$, where P_1 and P_2 are the pressures at T_1 and T_2 respectively. Subtracting the first equation from the second, we obtain

[1] Boltzmann, *loc. cit.*, p. 54.

$\frac{3}{2}(P_2 - P_1)V = 3(T_2 - T_1)$ and for a rise of temperature of 1° $\frac{3}{2}(P_2 - P_1)V = 3$ (calories). Therefore the molecular kinetic energy of a monatomic gas is increased by 3 calories for a rise of 1° in temperature, or, in other words, the molecular heat MC_v of a monatomic gas at constant volume is 3 calories. As the specific heat at constant pressure is $3 + 2 = 5$ calories, the ratio, MC_p/MC_v, for a monatomic gas must be 1·66, if the assumptions we have made on the basis of the kinetic theory are justified.

As has already been mentioned, C_v is somewhat difficult to determine directly, and to test the above deduction from the kinetic theory it is simpler to determine the ratio C_p/C_v indirectly, which can be done in various ways, for example, by measuring the velocity of sound in a gas. Kundt and Warburg (1876) therefore determined the velocity of sound in mercury vapour and obtained for the above ratio the value 1·66, in exact accord with the theoretical value, undoubtedly one of the most striking triumphs of the kinetic theory.

Conversely, a gas for which the ratio C_p/C_v is 1·66 must be monatomic, and by this method Ramsay showed that the rare gases argon and helium are monatomic.

For gases containing two or more atoms in the molecule, the heat supplied is employed not only in accelerating the rectilinear motion of the particles, but also in performing internal work in the molecule. As the former effect alone requires 3 calories, the total molecular heat of a polyatomic gas will be $3 + a$ calories, where a is a positive quantity, constant for any one gas. The value of MC_p will be $5 + a$ calories, and the ratio of the specific heats will be

$$\frac{MC_p}{MC_v} = \frac{5 + a}{3 + a} < 1{\cdot}67 > 1$$

less than 1·67 but greater than 1.

A comparison of the numbers given in the table shows that this deduction is in complete accord with the experimental facts. It may be expected that the more complex the molecule the greater will be the amount of heat expended in performing internal work and therefore the greater will be the specific heat. In accordance with this, MC_v for 1 mol of ether vapour is 33·5 calories, and for turpentine ($C_{10}H_{16}$) 66·8 calories.

The specific heat of monatomic gases is independent of temperature, that of polyatomic gases usually increases slowly with temperature.

While it may be anticipated, on the basis of the simple kinetic theory, that the molecular heat of a polyatomic gas will be greater than that of a monatomic gas, an extension of the theory is required in order to throw light on the heat capacity of polyatomic gases from a quantitative standpoint. This was first done by Clerk Maxwell and Boltzmann, who, with the aid of statistical mechanics, deduced the so-called *principle of equipartition of energy* and used it to calculate the molecular heat of diatomic and more complex gases. It has already been explained that the change of translational energy when a mol of gas (monatomic or polyatomic) is raised 1° in temperature at constant volume involves a heat capacity of 3 calories. In the case of diatomic gases, vibrational and rotational energy have also to be taken into account. For a diatomic gas, according to the principle of the equipartition of energy, translational and rotational energy together would give a heat capacity of 5 calories per mol per degree and when all three forms are included the calculated heat capacity is 7 calories per mol per degree at constant volume.

As is evident from the figures in the table on p. 52, the experimental values differ widely from those calculated according to the kinetic theory.

For triatomic gases, again, translation, vibration, and rotation should give a heat capacity of 12 calories per mol per degree. The molecular heat of water vapour at 100° is about 6 calories.

Moreover, the continuous variation of heat capacity with temperature for polyatomic gases cannot be explained on the principle of the equipartition of energy. This principle would involve either a constant molecular heat or an increase by steps as a new form of energy came into play.

A plausible explanation of these results has been proposed on the basis of the quantum theory. According to this theory, first put forward by Planck in connection with radiation, energy is not taken up continuously, but in definite increments, the so-called quanta. We assume, therefore, that rotational and vibrational energy are taken up in quanta and that it is

only under certain conditions that energy can be taken up. Thus Eucken has found that at $-238°$ the molecular heat of hydrogen has fallen to 3 calories—the same as for a monatomic gas, so that under these conditions it has neither vibrational nor rotational energy. It will be shown later (p. 155) that the results of measurements of the specific heat of solids, especially at low temperatures, cannot be reconciled with the classical kinetic theory and that in this case also the quantum theory has proved of value.

Experimental Illustrations—Experiments with gases are usually somewhat difficult to perform, and require special apparatus. Experimental illustrations of the simple gas laws are described in all text-books on physics, and need not be considered here.

The determination of the density[1] and hence the molecular weight of such a gas as carbon dioxide by Regnault's method may be performed as follows: One of the bulbs is first exhausted as completely as possible by means of a pump, the stop-cock closed, and the bulb weighed. It is then filled with water by opening the stop-cock while the end of the tube dips under the surface of water and again weighed. The volume of the bulb is obtained by dividing the weight of the water by its density at the temperature of the experiment. The water is removed from the bulb by means of a filter-pump, the interior of the bulb is dried (by washing out with alcohol and ether and warming), placed nearly to the stop-cock in a bath at constant temperature, the end is then connected to a T piece by means of rubber tubing; one of the free ends of the T piece is connected, through a stop-cock or rubber tube and clip, to a pump, the other, also through a stop-cock or rubber tube and clip, to an apparatus generating carbon dioxide. The bulb is evacuated by means of the pump, the stop-cock connecting it with the latter is then closed, that connecting it with the carbon dioxide apparatus opened, the bulb filled with carbon dioxide, disconnected and weighed. As the apparatus fills it with carbon dioxide at rather more than atmospheric pressure, the stop-cock is opened for a

[1] For full details as to the manipulation of gases, consult Travers' *Experimental Study of Gases* (Macmillan, 1901).

moment to adjust it to atmospheric pressure before weighing. The weight of a known volume of the gas at known temperature and pressure having thus been determined, its density and molecular weight can be readily calculated.

The determination of vapour densities by Victor Meyer's method is fully described on page 44, and may readily be performed by the student with ether or chloroform, steam being used as jacketing vapour.

CHAPTER III

LIQUIDS

General—Liquids, like gases, have no definite form, but, unlike the latter, they have a definite volume, which is only altered to a comparatively small extent by changes of temperature and pressure.

In contrast to the simple gas laws, the formulæ connecting temperature, pressure, and volume of liquids are very complicated and empirical in character, and depend also on the nature of the liquid. This is, of course, connected with the fact that liquids represent a much more condensed form of matter than gases. 1 c.c. of liquid water at 100°, when converted into vapour at the same temperature, occupies a volume of over 1600 c.c. It seems plausible to suggest that the main reason why the formulæ representing the behaviour of liquids are so much more complicated than the gas laws is that the mutual attraction of the particles, which is almost negligible in the case of gases (p. 40) is of predominant importance for liquids.

As is well known, gases can be liquefied by increasing the pressure and lowering the temperature; and, conversely, by raising the temperature and diminishing the pressure a liquid can be changed to a gas. It is shown in the next section that there is no difference in kind, but only a difference in degree, between liquids and gases.

Transition from Gaseous to Liquid State. Critical Phenomena—If gaseous carbon dioxide, below 31°, is confined in a tube and the pressure on it gradually increased, a point will be reached at which liquid makes its appearance in the tube, and the whole of the gas can be liquefied without appreciable increase of pressure. If, however, carbon dioxide above 31° is continuously compressed, no separation into two

layers (liquid and gas) occurs, no matter how high the pressure applied. Similarly, if carbon dioxide is contained in a sealed tube, under such conditions that both liquid and gas are present, and the temperature is gradually raised, it will be noticed that when the temperature reaches 31° the boundary between liquid and vapour disappears, and the contents of the tube become homogeneous. Other liquids show the same remarkable phenomena, but at temperatures which are characteristic for each substance. This temperature is known as the *critical temperature*; above its critical temperature no pressure, however great, will serve to liquefy a gas, below its critical temperature any gas can be liquefied by pressure. That pressure which is just sufficient to liquefy a gas at the critical temperature is termed the *critical pressure*, and the specific volume under these conditions is called the *critical volume*.

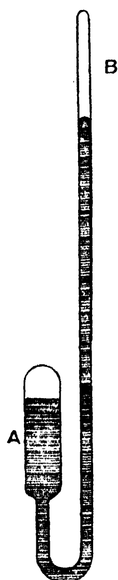


Fig. 3.

The critical phenomena may be observed, and rough measurements of the constants obtained, with an apparatus (Fig. 3) used by Cagniard de la Tour, who discovered these phenomena in 1822. The upper part of the branch A contains a suitable volume of the liquid to be examined, the branch B, the upper part of which is graduated, contains a little air to act as a manometer, the remainder of the apparatus (the shaded part in the figure) is filled with mercury. The tube at first contains both vapour and liquid, but on gradually raising the temperature, a point is ultimately reached at which the boundary between liquid and vapour becomes faint, and finally disappears; the tube is momentarily filled with peculiar flickering striæ, and then the contents become quite homogeneous. On allowing to cool, a mist suddenly appears in the tube at a certain temperature, and separation into liquid and vapour again occurs. The temperature at which the boundary disappears on heating or reappears on cooling approximates to the critical temperature, and the critical pressure can be calculated from the volume of air in B. As the temperature rises, the density of the liquid

in the sealed tube naturally decreases, whilst that of the vapour increases, and it has been shown that at the critical temperature the densities of liquid and vapour are equal.

There is also a close connection between surface tension and the critical temperature. As pointed out later (p. 89), the surface tension of a liquid is determined by the different degree to which molecules in the surface layer are attracted by liquid and vapour respectively. As the temperature rises, the difference in the densities of vapour and liquid and therefore the surface tension steadily fall, and at the critical temperature, when the densities of liquid and vapour are equal, the surface tension is zero.

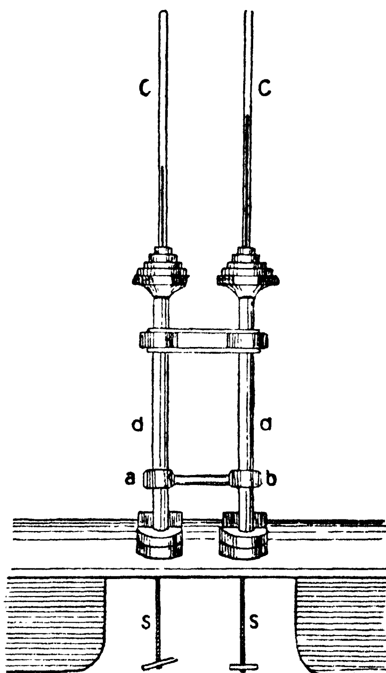


Fig. 4.

The compressibility of a gas can be measured, and the critical temperature and pressure determined with the apparatus designed by Andrews or the modified form used by Young.[1] The Andrews apparatus is illustrated in Fig. 4. The liquid or vapour to be examined is confined over mercury in a carefully calibrated capillary tube *c*, and a similar tube, containing air, is placed beside the experimental tube in order to measure the pressure. The capillary tubes are held in strong copper tubes *dd*, provided at the ends with brass flanges, and the lower ends of the capillary tubes dip in water with which the apparatus

[1] *Stoichiometry* (Longmans, Green & Co.), p. 132.

is filled. Lateral communication between the two tubes is provided by means of the connecting tube *ab*, and pressure is produced by screwing one or other of the steel plungers *ss* into the water.

The critical temperature can be determined by jacketing the tube and altering the temperature till the critical phenomena already described are observed. Observations are taken of the disappearance of the meniscus on heating and its reappearance on cooling; the mean is the critical temperature. The result does not depend on the volume of liquid in the tube.

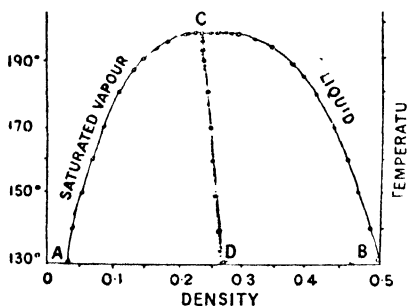


Fig. 5.

The critical pressure is obtained from the position of the mercury in the other tube when the experimental tube is at the critical temperature.

The critical volume is difficult to determine directly and is best obtained by applying the rule of Cailletet and Matthias that the mean of the densities of liquid and saturated vapour lie on a straight line, the so-called *rectilineal diameter*. In Fig. 5 the densities of liquid pentane and its saturated vapour are plotted at a series of temperatures up to a few degrees from the critical temperature. It is not possible to determine the densities up to the critical temperature, when they become equal, but

	Critical Temperature, C.	Critical Pressure (Atmospheres).
Helium . . .	− 267-268°	2·3
Hydrogen . . .	− 238°	15
Nitrogen . . .	− 149°	27
Oxygen . . .	− 119°	58
Carbon dioxide . .	31°	72
Ethyl ether . . .	195°	35
Ethyl alcohol .	243°	63

from the results at rather lower temperatures the curve can be completed with approximate accuracy. The point at which the rectilineal diameter, DC, when produced, intersects the curve is the critical density and its reciprocal is the critical volume.

The critical temperatures and pressures of a few substances are given in the table (p. 60).

Behaviour of Gases on Compression—We have already learnt that if gaseous carbon dioxide is compressed at a tem-

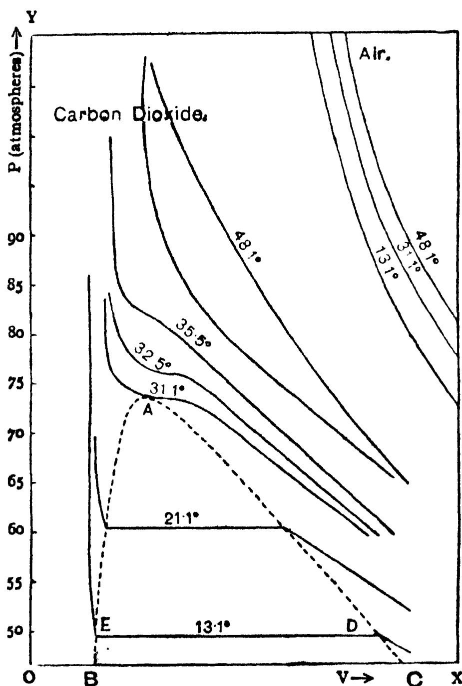


Fig. 6.

perature below 31° it can be liquefied, but if the compression is carried out above 31° no separation into two layers occurs. These relations are best shown diagrammatically, as in Fig. 6, in which the ordinates represent the pressures and the abscissæ the corresponding volumes at constant temperature. If the

gas in question obeys Boyle's law, the curves obtained by plotting the pressures against the corresponding volumes at constant temperature (the so-called isothermals) are hyperbolas, corresponding with the equation $pv =$ constant, and this condition is approximately fulfilled by air, as shown in the upper right-hand corner of the diagram. An examination of the isothermals for carbon dioxide shows that the same is nearly true of this gas at 48·1°, but at 35·5°, and still more at 32·5°, the isothermals deviate from those of an ideal gas. At the latter temperature it is very interesting to observe that the compressibility at 75 atmospheres is very great for a short part of the curve, and beyond that point extremely small; in the latter respect the highly compressed gas resembles a liquid. At the critical point, 31·1°, the curve is for a short distance practically horizontal, thus representing a great decrease of volume for a small change of pressure—in other words, a high compressibility. Finally, at 21·1° and 13·1°, separation of liquid takes place, the curves run horizontal whilst the gas is changing to liquid at constant pressure, and then the curves run almost vertical, indicating a small decrease of volume with increase of pressure (*i.e.*, a small compressibility), characteristic of liquids. It is evident from the foregoing that at any point *within* the dotted line ABC both vapour and liquid are present; at any point *outside* only one form of matter, either vapour or liquid.

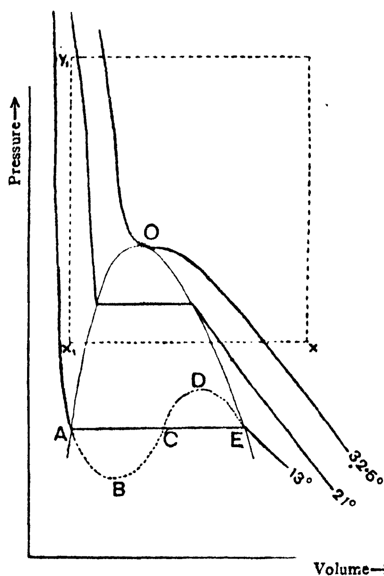


Fig. 7.

The above considerations serve to show that there is no fundamental distinction between gases and liquids: a highly-

compressed gas above its critical point cannot be definitely classified either as liquid or gas. It is evident from the figure that as regards compressibility, highly compressed carbon dioxide behaves more like a liquid than a gas. *It is, in fact, possible to pass from the typically liquid to the gaseous form, and vice versâ, without a separation into two layers.* Thus liquid carbon dioxide below 31°, under the conditions represented by the point x_1 in Fig. 7, may be compressed above its critical pressure along x_1y_1 and then warmed above its critical temperature whilst the pressure is kept constant at y_1. During this process no separation into two layers will be noticed, and by now reducing the pressure the fluid can be obtained in as dilute a form as desired (what is ordinarily termed a gas), say the condition represented by x, whilst remaining quite homogeneous. Similarly a gas can be completely converted to a liquid without discontinuity, along xyy_1x_1. Starting with a gas in the condition represented by x it is warmed at constant volume above the critical temperature to y, and then cooled at constant pressure till the volume is smaller than the critical volume, when we have a liquid.

Application of van der Waals' Equation to Critical Phenomena—We have already learnt that no actual gas follows the gas laws quite strictly, and, further, that the behaviour of actual gases can be represented with fair accuracy, even up to high pressures, by van der Waals' equation,

$$\left(\mathrm{P} + \frac{a}{\mathrm{V}^2}\right)(\mathrm{V} - b) = \mathrm{RT}.$$

If this equation is arranged in descending powers of V it becomes

$$\mathrm{V}^3 - \mathrm{V}^2\left(b + \frac{\mathrm{RT}}{\mathrm{P}}\right) + \mathrm{V}\frac{a}{\mathrm{P}} - \frac{ab}{\mathrm{P}} = 0 \ (1).$$

This is a cubic equation, V being treated as the variable and P and T, as well as a, b, and R, as constants. According to the conditions the equation has either three real roots or one real and two imaginary roots. Otherwise expressed, the magnitudes of a and b may be such that at one temperature and

pressure, the volume V has three real values, whilst at another temperature and pressure it may have only one real value. We will now compare these theoretical deductions with the actual case of carbon dioxide. It is clear from Fig. 6 that at 13·1° and 48 atmospheres, carbon dioxide has two volumes, as a gas (represented by the point D) and as a liquid (the point E), but the third volume demanded by the equation is not shown. At 48·1°, on the other hand, there is only one volume for each pressure, corresponding with one *real* root of the equation under these conditions.

Some light is thrown on the question of the missing third real volume when the isothermal curves for carbon dioxide are plotted by substituting the values of *a* and *b*, found experimentally (p. 40) in equation (1). The wavy curve ABCDE shown in Fig. 7 was obtained in this way; on comparison with the experimental curve for carbon dioxide (Fig. 6), it will be seen that whereas the points D and E in the latter isothermal for 13° are joined by a straight line DE, in the former the corresponding points E and A are joined by the dotted line ABCDE, *which represents a change from the gaseous to the liquid form without discontinuity.* The point C, at which the line of constant pressure cuts the isothermal, represents the third of the volumes required by the above cubic equation, but it probably cannot be realised in practice, as the part DCB of the curve on which it occurs represents decrease of volume with diminishing pressure, quite contrary to our usual experience. On the other hand, the sections AB and ED have a real meaning. When a vapour is compressed till saturated, it does not necessarily liquefy; in the complete absence of liquid it may be compressed considerably beyond the point at which liquefaction occurs in the presence of traces of liquid; in other words, a part of the curve ED may be experimentally realized. Similarly, water may be heated in a carefully cleaned vessel several degrees above its boiling-point, that is, it does not necessarily pass into vapour when the superincumbent pressure is less than its vapour pressure, and a part of the curve AB may thus be experimentally realized. Similar phenomena will be met with later; it often happens that when a system is under such conditions that the separation of another

phase (form of matter) is possible, the change does not occur in the absence of the new phase.

Van der Waals' equation can also be employed to obtain important relations between the critical constants and the other characteristic constants representing the behaviour of gases. It has already been pointed out that the densities and consequently the volumes of liquid and gas become equal at the critical temperature, and as this must also be true for the intermediate third volume, it follows that the three roots of the equation

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0 \ (1)$$

become equal under these conditions. If, in this general equation, we call the three roots V_1, V_2, and V_3, then the equation $(V - V_1)(V - V_2)(V - V_3) = 0$, must hold, which, when the roots are equal, becomes

$$(V - V_k)^3 = V^3 - 3V_kV^2 + 3V_k^2V - V_k^3 = 0 \ (2),$$

where V_k is the critical volume. Equating the coefficients of the identical equations (1) and (2), we have

$$b + \frac{RT_k}{P_k} = 3V_k \ (\text{i}); \quad \frac{a}{P_k} = 3V_k^2 \ (\text{ii}); \quad \frac{ab}{P_k} = V_k^3 \ (\text{iii}).$$

From the last three equations, the values of the critical constants can readily be obtained in terms of R, a, and b. We have

Critical volume $V_k = 3b$ (from ii and iii),

Critical pressure $P_k = \dfrac{a}{27b^2}$ (from ii),

Critical temperature $T_k = \dfrac{8a}{27Rb}$ (from i).

We thus reach the interesting result that the critical constants may be calculated from the deviations from the gas laws, when the latter are expressed in terms of the constants a and b of van der Waals' equation. As an illustration of the satisfactory agreement between the observed and calculated values, we will

take the data for ethylene, for which $a = 0{\cdot}00786$, $b = 0{\cdot}0024$, and $R = 0{\cdot}0037$.

$V_k = 0{\cdot}0072$ (observed value $0{\cdot}006$),

$$P_k = \frac{0{\cdot}00786}{27 \times (0{\cdot}0024)^2} = 50{\cdot}5 \text{ (observed value 51 atmospheres),}$$

$$T_k = \frac{8 \times 0{\cdot}00786}{27 \times 0{\cdot}0024 \times 0{\cdot}0037} = 262^\circ \text{ Abs. (observed value } 282^\circ\text{).}$$

Law of Corresponding States—Van der Waals has further pointed out that if the pressure, volume, and temperature of a substance are expressed as multiples of the critical values, that is, if we put $P = \alpha P_k$, $V = \beta V_k$, $T = \gamma T_k$, and then substitute in the equation $(P + a/V^2)(V - b) = RT$, P_k, V_k, and T_k being replaced by their values in terms of a, b, and R, the equation simplifies to

$$\left(\alpha + \frac{3}{\beta^2}\right)(3\beta - 1) = 8\gamma.$$

This equation does not contain the constants characteristic of any particular substance, and ought therefore to hold for all substances in the gaseous and liquid state. Experiment shows, however, that it is only to be regarded as a first approximation, the deviation in many cases being much greater than the experimental error.

For our present purpose, these considerations are chiefly of importance as affording information regarding the proper conditions for comparison of the physical properties of liquids. If we wish, for example, to compare the molecular volumes of ether and alcohol, it would probably not be satisfactory to compare them at the ordinary temperature of a room, as this would be near the boiling-point of ether, 35°, but much below that of alcohol, 78°. According to van der Waals, the proper temperatures for comparison, the so-called "corresponding temperatures," are those which are equal fractions of the respective critical temperatures. Thus, if we choose 20°, or 293° abs., as the temperature of experiment for ether, the critical temperature of which is 195°, or 468° abs., the proper temperature, t, for comparison with alcohol (critical temperature, 243° C.)

will be given by $\frac{273 + 20}{468} = \frac{273 + t}{516}$, whence $t = 51°$. The same considerations apply to the pressures.

The theoretical basis for this method of comparison is that as mentioned above, the choosing of pressures, volumes or temperatures which for different substances bear the same proportion to their respective critical constants leads, when substituted in van der Waals' equation, to an equation which is the same for all substances, and the practical justification for choosing these as corresponding conditions is that more regularities are actually observed by this method than when the comparison is made under other circumstances.

Liquefaction of Gases—As already indicated, all gases can be liquefied by cooling them below their respective critical temperatures and applying pressure. The methods employed for this purpose by Cailletet, Pictet, Wroblewski, and others are fully described in text-books of physics. In recent years the older methods have been almost completely displaced, in the case of the less condensable gases, such as air and hydrogen, by a method introduced almost simultaneously by Linde and by Hampson. The principle of the method is that when a gas is allowed to pass from a high to a low pressure through a porous plug, the resultant expansion (without external work) produces a cooling effect (Joule-Thomson effect). The cooling effect is due to the performance of *internal* work in overcoming the mutual attraction of the particles.

Apart from the cooling effect due to the performance of *internal* work there is a further effect, involving external work, due to deviations from Boyle's law. The effect is therefore dependent on the difference between p_2v_2, the product of pressure and volume on the low-pressure side, and p_1v_1 the corresponding product on the high-pressure side. For moderate changes of pressure, in the case of all gases except hydrogen and helium, p_2v_2 is greater than p_1v_1, external work is done resulting in a cooling effect, which is added to that due to internal work. In the case of hydrogen, however, p_2v_2 is less than p_1v_1 (p. 36), and therefore on expansion there is a heating effect which counteracts the cooling effect due to internal work. This accounts for the fact that at ordinary temperatures a

heating effect is observed when hydrogen expands through a porous plug. Below − 80° a cooling effect is obtained with hydrogen also.

The whole effect observed is therefore the algebraic sum of the effects arising from two different causes: (1) internal work against molecular forces, which always produces cooling; (2) external work, due to deviations from Boyle's law, which may result in heating or cooling. The first factor is the more important in connection with liquefaction of gases.

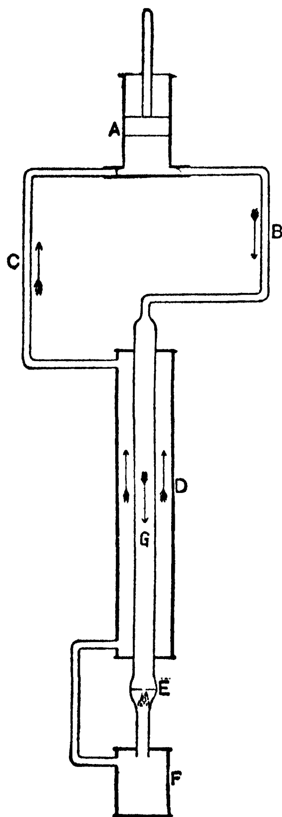


Fig. 8.

The cooling effect is the greater the lower the temperature at which the expansion takes place and the greater the difference of pressure on the two sides of the plug. The fall of temperature on expansion, θ, is given by the formula

$$\theta = n(p_1 - p_2)\left(\frac{273}{T}\right)^2$$

where $p_1 - p_2$ is the difference of pressure, T the temperature at which expansion occurs, and n a constant for the particular gas used. The cooling effects thus obtained are summed up in a very ingenious way by the principle of "contrary currents," the same quantity of gas being made to circulate through the apparatus several times, and after passing through the plug being caused to flow over and cool the tube through which a further quantity of gas is passing on its way to the plug (or small orifice).

The apparatus employed is represented diagrammatically in

Fig. 8. By means of the pump A, the gas is compressed in B to (say) 100 atmospheres, the heat given out in this process being absorbed by surrounding B with a vessel through which a continuous current of cold water is passed. The cooled, compressed gas then passes down the central tube G, towards the plug E, being further cooled on the way by the gas passing up the wide tube D, which has just expanded through the plug. After passing through E and thus falling to its original pressure, the gas passes upwards over the central tube G and again reaches A by the tube C, and the left-hand valve at the bottom of A. The direction of the circulating stream of gas is indicated by the arrows. In course of time, the temperature becomes so low that part of the gas is liquefied and collects in the vessel F. More air is drawn into the apparatus as required, and the process is continuous.

By means of an apparatus constructed on this principle, Dewar, and, somewhat later, Travers, succeeded in obtaining liquid hydrogen in quantity. All known gases have now been liquefied. The liquefaction of helium was first effected by Kammerlingh Onnes in 1908.

RELATION BETWEEN PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

General—The foregoing paragraphs of this chapter represent an introduction to the relationship between the physical properties of liquids and their chemical composition, inasmuch as information has been gained as to the conditions under which measurements should be made with different liquids in order to obtain comparable results (theory of corresponding states). Although in this chapter we are mainly concerned with the physical properties of pure liquids, it is convenient to include also some observations with solutions. We will deal shortly with the following physical properties: (1) Atomic and molecular volumes; (2) refractivity; (3) rotation of plane of polarisation of light; (4) absorption of light; (5) viscosity.

Atomic and Molecular Volumes—In the case of gases, we have seen that simple relations are obtained when the volumes occupied by different substances in the ratio of their molecular weights are compared; at the same temperature and pressure

the volumes are equal. The justification for taking the molecular weights (in grams, for instance) as comparable quantities is that, according to the molecular theory, equal numbers of molecules of different substances are thus compared. Similarly, in dealing with liquids, it is usual to determine the *molecular volume* of the liquid, *i.e.*, the volume occupied by the molecular weight of the liquid in grams, which is, of course, obtained by dividing the molecular weight in grams by the density of the liquid at the temperature of experiment. As the specific volume, v, of a liquid is inversely as the density, the molecular volume may also be defined as molecular weight in grams × sp. volume. Similarly, the atomic volume = (atomic weight in grams) ÷ density, or (atomic weight in grams) × sp. volume.

Kopp was the first chemist to carry out an extended series of observations on this subject, and he found that the most regular results were obtained when molecular volumes were determined, not at the same temperature, but at the boiling-points of the respective liquids under atmospheric pressure. It is interesting to observe that this purely empirical method of procedure was found much later to be theoretically justifiable, as the boiling-points of most liquids are approximately two-thirds of their respective critical temperatures (both measured on the absolute scale). The boiling-points are therefore corresponding temperatures (p. 66).

Kopp found that as a first approximation the molecular volume could be regarded as the sum of numbers representing the volumes of the component atoms. The atomic volumes of the commoner elements occurring in organic compounds are as follows:—

C	H	Cl	Br	I	S	O(O—H)	O(O=)
11	5·5	22·8	27·8	37·5	22·6	7·8	12·2

In some cases the atomic volume depends on the way in which the element is bound, thus oxygen joined to hydrogen (hydroxyl oxygen) has the atomic volume 7·8, whilst for oxygen doubly linked to carbon (carbonyl oxygen) the volume is 12·2. As an illustration the calculated and observed volumes of acetic acid may be compared as follows:—

$$
\begin{aligned}
2C &= 22 \\
4H &= 22 \\
\text{(Carbonyl) O} &= 12{\cdot}2 \\
\text{(Hydroxyl O} &= 7{\cdot}8 \\
\hline
& \quad 64{\cdot}0
\end{aligned}
$$

As the molecular weight of acetic acid is 60 and its density at the boiling-point is 0·942 the observed molecular volume $M/d = 63{\cdot}7$.

It should be mentioned that the atomic volumes given above are not obtained directly, but by comparison of chemical compounds with definite differences of composition (*e.g.*, the difference in the molecular volumes of the compounds C_4H_{10} and C_4H_8 gives the volume of two atoms of hydrogen), and are therefore not necessarily the same as those for the free elements. In some cases, however, the two values coincide, thus the atomic volumes of the free halogens, chlorine and bromine, at their boiling-points are 23·5 and 27·1 respectively, whilst their values in combination are 22·8 and 27·8, so that the halogens have approximately the same volume in the free and combined condition. The same is approximately true for certain other elements for which comparison is possible.

The extended investigations of Thorpe, Lossen, and Schiff afford a general confirmation of Kopp's conclusions; the calculated and observed values generally agree within about 4 per cent.

Although, strictly speaking, the consideration of the molecular volume of a substance in solution does not belong to this section, it is convenient to refer to it here. The *molecular solution volume*, Mv, of a substance may readily be calculated from the formula $Mv = \frac{M + n}{d} - \frac{n}{d'}$, where M is the molecular weight of the solute in grams, n the weight of the solvent containing M grams of solute, d the density of the solution, and d' that of the solvent. This formula is derived on the assumption, which is certainly not justifiable, that the density of the solvent itself is not affected by dissolving a substance in it, and therefore Mv is only the "apparent" solution volume. The molecular volume

is sometimes nearly the same in the free state and in solution [1] (*e.g.*, bromine in carbon tetrachloride), but is often much less (*e.g.*, many salts in water).

Additive, Constitutive and Colligative Properties—The molecular volume is a good example of what is termed an *additive* property, since it can be represented as the sum of volumes pertaining to the component atoms. It is not, however, strictly additive, since it is influenced somewhat by the arrangement of the atoms in the molecule, and therefore the atoms to some extent influence each other. Properties which depend largely on the constitution of the molecule, in other words, on the arrangement of the atoms in the molecule, are termed *constitutive*; a typical constitutive property is the rotation of the plane of polarization of light (p. 75). The only strictly additive property is weight. Other properties, such as the refractivity, the molecular volume, heat of combustion, etc., are more or less additive, but are to some extent complicated by constitutive influences, probably due largely to the mutual influence of the atoms.

There is a third class of properties, which always retain the same value independent of the *number and nature* of the atoms in a molecule or of their arrangement, and depend only on the number of molecules. A good illustration of these properties has already been met with in connection with gases. When these are taken in quantities which, according to the atomic theory, are proportional to their molecular weights, they all exert the same pressure when occupying equal volumes at the same temperature. Such properties have been termed *colligative* by Ostwald.

Many illustrations of these three classes of properties will be met with in the course of our work.

Refractivity—The velocity with which light is propagated through different substances is very different. The relative velocities in two media can be deduced when the change in direction of a ray of light in passing from one medium to another is known. When the ray passes from one medium to the other, the incident ray, the refracted ray (in the second medium) and the normal to the boundary between the two

[1] Lumsden, *Trans. Chem. Soc.*, 1907, **91**, 24; Dawson, *ibid.*, 1910, **97**, 1041.

media (a line drawn perpendicular to the boundary where the incident ray meets it) are in one plane. If i is the angle of incidence (the angle between the incident ray and the normal) (Fig. 9) and r is the angle of refraction (the angle between the normal and the refracted ray) and v_1 and v_2 the respective velocities of light in the two media, it can be shown that the ratio of the sine of the angle of incidence to the sine of the angle of refraction is constant, and is equal to the ratio of the velocity of light in the two media. The ratio in question is termed the *index of refraction*, and is usually represented by the symbol n. We have therefore the relation

$$n = \frac{\sin i}{\sin r} = \frac{v_1}{v_2}.$$

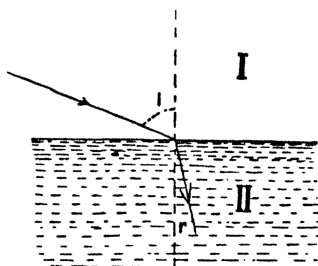


FIG 9.

If the first medium is a vacuum, n is always greater than 1—in other words, light attains its greatest velocity in a vacuum, and is retarded on passing through matter. The refractive index is, however, often referred to air as unity, and to convert the values thus found to a vacuum they must be multiplied by 1·00029, giving what is termed the "absolute refractive index".

An instrument employed for the determination of refractive indices is termed a refractometer. Among the more convenient forms of refractometer, those due to Abbé and to Pulfrich may be specially mentioned.

Ordinary white light cannot be employed for refractivity measurements, as the component rays are refracted or retarded to a different extent on passing through matter, the rays thus scattered or *dispersed* giving rise to a spectrum. This difficulty is avoided by using light of the same wave-length (so-called monochromatic light), and for this purpose sodium light, the wave-length of which is represented by the letter D, is convenient. Measurements of the refractive index referred to sodium light are represented by the symbol n_D.

The refractive index of a given substance, like any other

property, depends on the conditions of temperature, pressure, etc., under which the measurements are made. It has been found convenient to express the results of measurements not simply in terms of n_D, but in terms of the function $\frac{n - 1}{d}$ where d is the density of the liquid or gas (Gladstone and Dale, 1858). This purely empirical function, known as the refraction constant,[1] is, for any given substance, practically independent of the temperature. In 1880, Lorenz and Lorentz arrived simultaneously, from theoretical considerations, at the somewhat more complicated expression, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$, and showed that, for the same substance, it remained fairly constant, not only for widely differing temperatures, but even for the change from liquid to gaseous form. Thus Eykman found that the value of this function for isosafrol, $C_{10}H_{10}O_2$, amounted to 0·2925 and 0·2962 at 17·6° and 141° respectively, and Lorenz obtained for water at 10° and water vapour at 100° the values 0·2068 and 0·2061 respectively.

For comparative purposes, it is usual to employ the *atomic refraction* (atomic weight × refraction constant) and the *molecular refraction* (molecular weight × refraction constant); the latter, if we employ the second form of the refraction constant, is given by $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$, where M is the molecular weight. In this case also it has been found, from measurements on many organic liquids, that the molecular refraction may be represented to a first approximation as the sum of the refractions of the component atoms, so that the refractive power is largely an additive property.

Just as in the case of molecular volumes, however, there are certain deviations from this additive behaviour (constitutive influences) which may be connected with the arrangement of the atoms in the molecule. Brühl,[2] who has been particularly prominent in investigating this question, points out that the

[1] The expression here called the "refraction constant" is sometimes called the "specific refractivity".

[2] For a short summary of Brühl's work, by himself, see *Proc. Royal Institution*, 1906, **18**, 122.

molecular refraction of compounds containing double and triple bonds is greater than the calculated value, and he takes account of this constitutive influence by ascribing definite refractivities to these bonds. The most recent values for a few of the elements are as follows:—[1]

C	H	Oxygen (in CO group)	Oxygen (in ethers)	Oxygen (in OH group)	Cl	I	Double bond	Triple bond
2·418	1·100	2·211	1·643	1·525	5·967	13·90	1·733	2·398

Later investigations show that neighbouring double or triple bonds exert a mutual influence, so that the matter becomes somewhat complicated.

Conversely, it is sometimes possible, from measurements of the refractive index (or other physical property), to draw conclusions as to the constitution of chemical compounds, but as our knowledge of the relations between physical properties and chemical constitution is very imperfect, this method should only be employed with great caution. It is evident that no conclusions as to chemical constitution can be drawn from additive properties, but only from constitutive properties.

Rotation of Plane of Polarization of Light—The properties of liquids so far dealt with have been mainly additive, the magnitude of properties such as volume, effect on the speed of light, etc., being much the same in the free state and in combination. We have now to deal with the property possessed by a few liquids (and dissolved substances) of rotating the plane of polarized light—a property which depends entirely upon the arrangement of the atoms in the molecule. Isomeric substances have in general nearly equal molecular refractivity and molecular volume, but it often happens that of two isomeric substances, such as the two lactic acids, one rotates the plane of polarized light and the other does not.

Plane polarized light (light in which the vibrations are all in one plane) is obtained by passing monochromatic light through a polarizing prism (Nicol prism or tourmaline plate) which cuts off all the rays except those vibrating in one plane. A prism of this type is mounted at some distance from another similar prism in such a way that light which has been polarized in the

[1] The numbers are referred to the D line (sodium light) and are calculated according to the Lorentz formula.

first prism may be examined after it has passed through the second prism, which is termed the analyser. If now the analyser is rotated until it is perpendicular to the polarizer, all the light which passes through the former will be cut off by the analyser, and on looking through the eyepiece the field will appear dark. If now, while the prisms are in this relative position, a tube filled with turpentine is placed between them, the field again appears clear, but becomes dark on rotating the analyser through a certain angle. This observation is readily accounted for on the view that the plane of polarization is twisted through a certain angle whilst the light is traversing the turpentine, and the analyser must therefore be rotated in order to bring it into the former relative position with regard to the polarized ray. The angle through which the analyser has been turned is read off on a graduated scale. The instrument used for measuring the rotation of liquids, which consists essentially of the two prisms and graduated scale, as described above, is termed a polarimeter. The observed angle of rotation depends on the nature of the liquid, on the wave-length of the light employed in the measurements, and on the temperature, and is proportional to the length of liquid traversed. For purposes of comparison, the results are usually expressed in terms of the *specific rotation* $[\alpha]$ for a fixed temperature, t, and a particular wave-length of light (for example, sodium light) by means of the formula

$$[\alpha]_D^t = \frac{\alpha}{ld},$$

where α is the observed angle, l is the length of the column of liquid in decimetres, and d is the density of the liquid at the temperature t. The *molecular rotation* $m[\alpha]$ is obtained by multiplying the specific rotation by the molecular weight of the liquid.

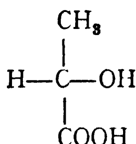
The specific rotation of substances in solution is represented by the analogous formula

$$[\alpha]_D^t = \frac{100\alpha}{gld},$$

where g is the number of grams of solute in 100 grams of the

solution, d is the density of the solution at the temperature t, and α and l have the same significance as before.

The liquids and dissolved substances which possess this remarkable property are almost exclusively compounds containing carbon. Further, only compounds containing an asymmetric carbon atom, that is, a carbon atom joined to four different groups, have the power of rotating polarized light (van't Hoff and Le Bel, 1874). For example, the graphic formula of ordinary lactic acid, which is optically active, may be written as follows :—



showing that no two of the groups attached to the central carbon atom are identical. A further remarkable fact is that when one form of a substance, such as lactic acid, can rotate the plane of polarized light to the right, a second modification can always be obtained which, although identical with the first in all other physical properties, rotates polarized light to the left to the same extent as the first modification rotates it to the right. The first is termed the *dextro* or *d* modification, the second the *laevo* or *l* modification. Van't Hoff and Le Bel account for this on the hypothesis that the four different groups are not in the same plane as the carbon atom, but are arranged in the form of tetrahedron with the carbon atom in the centre. It can be shown, most readily by means of a model,[1] that when all four groups are different there are two arrangements which cannot be made to coincide by rotating one of the models. These two arrangements behave to each other as object and mirror image, or a right- and left-hand glove, which cannot be brought into the same relative position, and, according to the theory, correspond with the *dextro* and *laevo* modifications respectively. If any two of the groups become identical, however, the two arrangements can always

[1] Models for this purpose can be bought for a few pence, or can be made by the student with a piece of cork and four pins provided with differently coloured balls at the ends.

be brought to coincidence, and there is no possibility of optical isomerism.

In calculating the specific rotation of a dissolved substance, it is implicity assumed that it is not affected by an indifferent solvent. As a matter of fact, however, the molecular rotation of a dissolved substance often differs considerably from its value in the pure state. This is well shown by the following results obtained by Patterson[1] for *l*-menthyl-*d*-tartrate in the pure state, and in 1·2 per cent. solution.

Molecular Rotation of *l*-menthyl-*d*-tartrate.

Solvent.	*Molecular Rotation at* 20°
None	– 284°
Ethyl alcohol	– 306·2°
Benzene	– 296·1°
Nitrobenzene	– 245·3°

So far, no definite connection has been found between any other property of the solvent and its effect on the rotation of a solute. Almost the only regularity which has yet been discovered in this branch of the subject is that the rotatory power of the salt of an optically active acid (or base) in dilute solution is independent of the nature of the base (or acid) with which it is combined. This important result is further referred to at a later stage.

All transparent substances, when placed in a magnetic field, rotate the plane of polarized light, and the late Sir William Perkin, who devoted many years to the systematic investigation of this subject, showed that this *magnetic rotation* is, like refractivity, largely an additive property.

Absorption of Light[2]—When a ray of white light passes through matter a greater or less amount of absorption invariably occurs, and the spectrum of the issuing ray shows dark bands corresponding with the rays which have been absorbed. This spectrum is termed an *absorption spectrum*. Absorption may be general or selective. In the former case there is a

[1] See *Trans. Chem. Soc.*, 1905, **87**, 128.

[2] Smiles, *Chemical Constitution and some Physical Properties* (Longmans, 1910), pp. 324-423.

general weakening throughout whole regions of the spectrum; in the latter case, there are independent relatively narrow bands in different regions of the spectrum.

The absorption spectrum is one of the most characteristic properties of a given substance or class of substances under definite conditions. Thus, for instance, the absorption spectra of permanganates in dilute solution are characterised by the presence of five dark bands in the green.

In the case of liquids or solutions, absorption is most conveniently measured in the transmitted light, as already indicated. In the case of solids, however, observations may be made with reflected light, as part at least of the reflection takes place from layers a little below the surface, and the short distance traversed is usually sufficient to produce some absorption.

The method which is most largely employed in the case of liquids is to use as a source of illumination the electric arc or spark passing between metallic (preferably iron) poles, the spectrum of the light being photographed after the latter has passed through the liquid. Substances which have high absorbing power are usually examined in solution, and the solvent chosen should not itself show absorption in the part of the spectrum studied. Ethyl alcohol is most largely used as solvent.

A very important question in such measurements is the effect of dilution on the persistence and intensity of a band—it very often happens that a band appears only within certain limits of dilution. For this reason, it is usual to carry out measurements with varying thicknesses of the absorbing layer and with varying concentrations. The solutions are made more and more dilute till absorption is no longer observed. For purposes of comparison, the solutions to be examined are usually made up to contain simple fractions of a mol per litre.

The method usually employed in representing the results graphically requires some explanation. It is illustrated in Fig. 10, which shows the absorption in the ultra-violet region of a solution of the amino derivative of dimethyldihydroresorcin in ethyl alcohol. The diagram shows the presence of one band. The principle of the method is that the oscillation frequencies of the limits of the absorption band are plotted *against the logarithms of the relative thicknesses referred to*

the thinnest layer of the most dilute solution examined. It is more convenient to use the logarithms of the relative thicknesses than the thicknesses themselves as ordinates. The latter are shown on the right-hand side of the figure, and it is evident that if equal increments of thickness were used, the curve would become inconveniently long. The space above the curve shows the wave-lengths of the light absorbed at different dilutions, and the curve itself represents the limits of the absorption. The lowest part of the curve, usually termed the "head," is that point at which the strongest absorption takes place; in the diagram it occurs at an oscillation frequency of 3600 units. The so-called "persistence" of the band is the difference of the logarithms of the thicknesses at which the band makes its appearance and disappears respectively, and is indicated on the diagram by its depth (in the present case extending from 1 to 23 units).

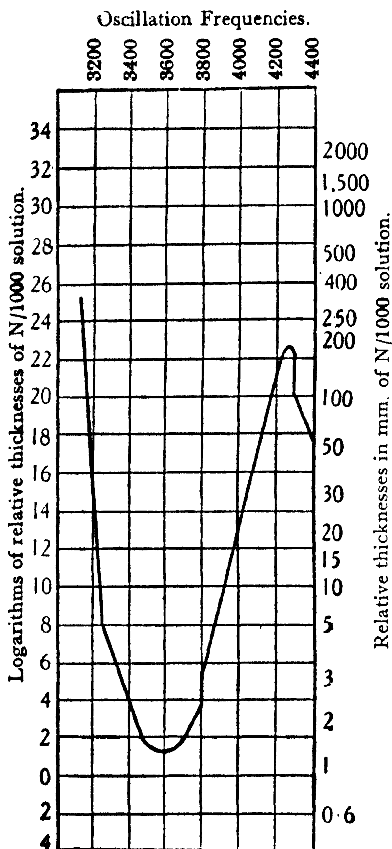


FIG. 10.

It may be mentioned that most of the measurements have been made in the ultra-violet region of the spectrum, but a certain number of observations have also been made in the visible and ultra-red regions.

A great deal of discussion has taken place as to the mechanism of light absorption, and a dynamical explanation has found most favour. According to Drude, absorption in the ultra-violet and visible regions is connected with the presence of negative electrons (valency electrons), and there is doubtless some intimate connection between the rate of vibration of the electrons and the frequency of the light waves absorbed. It appears, however, that absorption in the ultra-red region is due, not to electrons, but to particles of much greater magnitude, probably atoms or even groups of atoms.

As already indicated, the absorption spectra of chemical compounds are closely related to their constitution, and in recent years this method of elucidating chemical constitution has come increasingly into use. The progress made in this branch of investigation is mainly due to Hartley, and within the last few years to Baly and his co-workers.[1] It is impossible here to do more than to indicate in the briefest way the broad differences between the absorption spectra of the main groups of organic compounds.

According to Hartley,[2] all compounds which exert selective absorption are of aromatic character, for example, benzene, pyridine, and their derivatives. Those showing strong general absorption have also a cyclic structure, but are not typical aromatic compounds; examples, thiophene, piperidine, etc. Finally, compounds which exert only a weak general absorption are open chain compounds; examples, fatty alcohols, esters, etc. Although recent investigation has led to the discovery of one or two exceptions to these generalizations, they remain substantially accurate.

Apart from these broad differences in the absorption curves of different groups of organic compounds, it has been shown by Hartley that substances of closely allied constitution have absorption curves of similar type. The recent progress in the establishment of the chemical constitution of organic compounds from measurements of their absorption spectra is entirely due to the application of this important rule. Thus if the constitution of one compound is known with certainty from its

[1] *Trans. Chem. Soc.* from 1904 onwards.
[2] British Association Report, 1903.

chemical behaviour, and a second compound can be represented by alternative formulæ, of which one is analogous to that of the compound of known constitution, a comparison of absorption spectra often enables a decision to be made.

Like the other physical methods of determining chemical constitution, the one under discussion should be used with considerable caution in the present very imperfect state of our knowledge of absorption phenomena. As a supplement to purely chemical methods of determining constitution, however, especially when such methods lead to contradictory results, it is rendering valuable service.

As regards the additive character of absorption spectra, comparatively little is known with certainty. The determination of the effect of different groups of atoms on the character of the absorption spectrum is attended with considerable difficulty, but some progress has been made in this direction. Ultra-red absorption spectra have a pronounced additive character; this is probably connected with the generally accepted view that absorption in this case is connected with the vibrations of the atoms themselves.

Viscosity—The measurement of internal friction, or viscosity, gives information as to the work done in the relative displacement of the particles of a solid, liquid, or gas. In the case of liquids, for which the property has been most fully investigated, the viscosity is most conveniently studied by observing the rate of flow through capillary tubes. We may assume that the layer of liquid in contact with the wall of the tube is at rest, that the layer next to it is moving slowly parallel to the axis of the tube, and that the rate of movement gradually increases towards the interior, attaining its maximum at the centre of the tube. It is evident that the rate of displacement of the layers with regard to each other must be mainly determined by the amount of friction between them, and hence measurements of the rate of flow afford information as to the viscosity of liquids. The converse of viscosity is termed *fluidity*; a liquid of small viscosity, such as ether, is said to have a high degree of fluidity.

The magnitude of the viscosity depends greatly on the nature of the liquid. Thus the viscosity of warm ether is

very small, whereas that of treacle and of pitch is so great that they approximate to the behaviour of solids, the internal friction of which is extremely high. The internal friction of gases is very small (p. 32).

The *coefficient of viscosity*, η, is usually defined as the force required to move a layer of unit area in unit time through a distance of unit length past an adjacent layer unit distance away. For water at 15°, $\eta = 0{\cdot}0134$ in absolute units; for glycerine at the same temperature, $\eta = 2{\cdot}34$.

The coefficient of viscosity of a liquid can be calculated from the rate of outflow from a cylindrical tube by means of the equation

$$\eta = \frac{p\pi r^4 t}{8lv},$$

where v is the volume of liquid discharged in the time t, p the pressure under which the outflow takes place, r the radius and l the length of the tube. In practice, however, the rate of flow of the liquid is compared with that of a standard liquid, usually water, under the same experimental conditions, and its absolute viscosity, η, calculated by means of the formula

$$\eta/\eta_\omega = t/t_\omega,$$

where η_ω is the absolute viscosity of water at the temperature of the experiment, and t and t_ω are the times required for the discharge of equal volumes of the liquid and water respectively.

The viscosity of liquids diminishes rapidly as the temperature rises, but so far no simple relationship of general applicability connecting change of viscosity and temperature has been discovered.

Measurement of Viscosity—The determination of viscosity by the comparative method may be conveniently carried out with the apparatus described by Ostwald and illustrated in Fig. 11. It consists essentially of a capillary tube, *db*, connected at its upper part with a bulb, *k*, and at its lower end with a wider tube, bent into U-shape and provided with a bulb, *e*. Marks are etched on the capillary tube at *c* and *d* above and below the bulb *k*. The apparatus is filled at *f* with a definite volume

of the liquid, which is then sucked into the other limb till the surface rises above the mark *c*. The time required for the level of the liquid to fall from *c* to *d* is then noted. Observations have previously been made with water under similar conditions. As the pressures under which the discharge takes place are in the ratio of the density, *d*, of the liquid to that of water, the relative viscosity, $x = \eta/\eta_w$ is given by the equation

$$x = dt/d_w t_w.$$

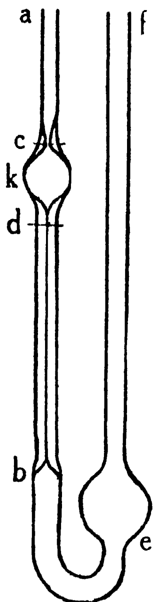


FIG. 11.

On account of the great influence of temperature on the viscosity, the measurements must be made at constant temperature, and for this purpose the apparatus is so constructed that it can conveniently be immersed in a thermostat.

Results of Viscosity Measurements[1]—Reference has already been made to the enormous differences in the viscosity of liquids, and also to the fact that temperature has a great influence on the magnitude of the viscosity. In comparing different liquids with regard to viscosity, we are again confronted with the difficulty of deciding at what temperatures the measurements should be made. The choice of the boiling-points as corresponding temperatures (p. 70) did not in this case lead to very satisfactory results, and most regularities were observed by using the data for points at which the rate of change of viscosity with temperature is the same (Thorpe and Rodger).

A comparison of substances of allied chemical constitution shows that viscosity is to some extent an additive property, but is greatly affected by constitutive influences.

The absolute viscosity of a number of pure liquids at 0° and at 25° is given in the accompanying table (Walden) :—

[1] Smiles, *loc. cit.*, pp. 51-105.

Liquid.	η at 0°.	η at 25°.
Acetone	0·00397	0·00316
Methyl alcohol	0·00846	0·00580
Acetic anhydride	0·0130	0·00860
Water	0·0178	0·00891
Ethyl alcohol	0·0179	0·0108
Benzonitrile	0·0194	0·0125
Nitrobenzene	0·0307	0·0182

In recent years the viscosity of mixtures of liquids has been the subject of a good deal of investigation. If for simplicity we confine our attention to mixtures of two components only, three classes may be distinguished :—

(1) The viscosity of the mixture lies between those of the pure components. Example, ethyl alcohol and carbon disulphide.

(2) The viscosity of the mixture in certain proportions is greater than that of either component. Example, pyridine and water.

(3) The viscosity of the mixture in certain proportions is less than that of either constituent. Example, benzene and acetic acid.

A few numbers illustrating the behaviour of the mixtures cited as examples of classes (2) and (3) are given in the accompanying table :—

Pyridine and Water.[1]		Benzene and Acetic Acid.[2]	
Per cent. Pyridine.	η at 25°.	Per cent. Benzene.	η at 25°.
0·00	0·00890	0·00	0·01174
19·28	0·01336	34·93	0·00734
39·84	0·01833	48·29	0·00666
59·70	0·02187	77·26	0·00597
66·65	0·02225	89·73	0·00591
80·15	0·01894	97·25	0·00594
100·00	0·00885	100·00	0·00598

[1] Hartley, Thomas, and Appleby, *Trans. Chem. Soc.*, 1908, 94, 538.
[2] Dunstan, *ibid.*, 1905, 87, 16.

The results are very similar to those for the vapour pressures of binary mixtures, described later (p. 99).

No general agreement has so far been reached as to the explanation of these remarkable differences in the behaviour of binary mixtures (compare p. 343).

Measurements of the viscosity of salt solutions (solutions which conduct the electric current) have also led to interesting results, but they cannot be usefully considered at the present stage.

Molecular Weight of Liquids—Our knowledge as to the molecular weight of pure liquids is due mainly to the investigations of Eötvös (1886) and of Ramsay and Shields (1893), and is based on the remarkable rule, discovered by Eötvös, that *the rate of change of the "molecular surface energy" of many liquids with temperature is the same.* If γ represents the surface tension and therefore the energy per sq. cm. of surface and s the "molecular surface," the rule in question may be written

$$\frac{d(\gamma s)}{dt} = c \quad . \quad . \quad . \quad . \quad (1)$$

where c is a constant.[1] The molecular surface, s, can be ex-

[1] The student should make himself familiar with this method of representing rate of change, as it is largely used in physical chemistry. It is perhaps most readily understood by considering the rate of change of position of a body as discussed in mechanics. If a body is moving with uniform velocity, the velocity can at once be found by dividing the distance, s, traversed by the time, t, taken to traverse it, hence velocity $= \frac{s}{t}$. The velocity may, however, be continually altering, and it is often desirable to express the velocity at any instant. It is not at first sight evident how this can be done, as it requires *some* time for the particle to traverse any measurable distance, and the velocity may be altering during that time. The nearest approach to the real velocity at any instant will be obtained by taking the time, and therefore the distance traversed, as small as possible. We might then imagine an ideal case in which s and t are taken so small that any error due to the variation of speed during the time t can be neglected. If we represent *these* values of s and t by ds and dt respectively, the speed of the particle at any instant will be given by ds/dt.

In the example given in the text, $d(\gamma s)/dt$ represents the rate of change of the product with temperature, and the equation shows that the rate of change is constant.

pressed in terms of readily measurable quantities as follows: The molecular volume of any liquid is represented by Mv, where M is the molecular weight and v the specific volume. If the molecular volume is regarded as a cube, one edge of the cube will measure $(Mv)^{1/3}$, and the area of one side of it $(Mv)^{2/3}$. $(Mv)^{2/3}$ may therefore be called the molecular surface, s, and just as the relative molecular volumes of different liquids contain an equal number of molecules so the relative molecular surfaces for different liquids are such that an equal number of molecules lie on them. Equation (1) then becomes

$$\frac{d[\gamma(Mv)^{2/3}]}{dt} = c, \text{ or } \frac{\gamma_1(Mv_1)^{2/3} - \gamma_2(Mv_2)^{2/3}}{t_1 - t_2} = c \quad . \quad (2)$$

where γ_1 and γ_2 are the surface tensions of a liquid at the temperatures t_1 and t_2 respectively. From equation (2) we obtain, for the molecular weight M,

$$M = \left\{\frac{c(t_1 - t_2)}{\gamma_1 v_1^{2/3} - \gamma_2 v_2^{2/3}}\right\}^{3/2} \quad . \quad . \quad . \quad (3)$$

The surface tension of a large number of pure liquids at different temperatures has been measured by Ramsay and Shields by observing the height to which they rose in capillary tubes. The results show that, if M is taken as the molecular weight corresponding with the simplest formula of the liquid, the value of c for the majority of substances is about — 2·12.

The method may be illustrated [1] by a determination of the molecular weight of liquid carbon disulphide. The experimental data are that $\gamma = 33·6$ ergs per sq. cm. at 19·4°, and 29·4 ergs at 46·1°: the specific volume (1/density) of carbon disulphide at 19·4° is 1/1·264; at 46·1° it is 1/1·223. Hence

$$M = \left\{\frac{-2·12(19·4 - 46·1)}{33·6/(1·264)^{2/3} - 29·4/(1·223)^{2/3}}\right\}^{3/2} = 81·5$$

as compared with the value 76 calculated from the formula.

As already indicated, the surface tension of a liquid in contact with its vapour diminishes as the temperature rises and

[1] Ramsay and Shields, *Trans. Chem. Soc.*, 1893, 63, 1006.

becomes zero at the critical temperature, where the surface of separation between liquid and vapour disappears (p. 59). If temperatures are measured downwards from the critical temperature as zero, dt in equation (1), p. 86, has a positive value, and therefore c is positive. In the next section for convenience positive values of the constant will be used. It should be added that the rule regarding the constancy of the expression $d(\gamma s)/dt$ only holds for temperatures at some distance (say 50°) below the critical temperature.

Results of Measurements—Among the liquids which give values for c about 2·12 are the following: benzene 2·17, carbon tetrachloride 2·11, silicon tetrachloride 2·03, ethyl iodide 2·10, ethyl ether 2·17, benzaldehyde 2·16, aniline 2·05. On the other hand, many substances give values for c which are much smaller than 2·12 and which vary with the temperature. Thus for ethyl alcohol the values of $d[\gamma(Mv)^{2/3}]/dt$ in the neighbourhood of the temperatures indicated are as follows: 1·18 at 30°, 1·31 at 90°, 1·46 at 130°, 1·77 at 185° and 1·94 at 225°. Among substances which give low values for c are the alcohols, the organic acids (acetic acid 0·90 at 16-46°), acetone and water.

The most plausible explanation of these observations is that liquids which give constant values for c approximating to 2·12 are non-associated, whilst those giving smaller values for this factor are associated. We may assume that association would tend to lower the molecular volume and thus give a smaller value for c, as is actually found. The fact that for liquids with abnormally small values for c the latter increases steadily with the temperature is also in harmony with this explanation, since it may be assumed that the molecular complexity diminishes with rise of temperature.

Attempts have been made to deduce from the observed values of $d(\gamma s)/dt$ the degree of complexity of associated liquids, but the results are by no means conclusive. According to Ramsay, the association factor of water at 5°, 25°, 45°, and 85° is 3·81, 3·44, 3·13, and 2·79 respectively; van der Waals, however, deduces from the same data considerably smaller values for this factor.[1] It is quite certain that water under ordinary

[1] *Zeitsch. Physikal. Chem.*, 1894, **13**, 713. See also General Discussion, *Trans. Faraday Soc.*, 1910, **6**, 71-123.

conditions is a complex mixture of molecules of the formulæ H_2O, $(H_2O)_2$, $(H_2O)_3$ and perhaps still more complicated aggregates, but the average degree of association at any given temperature is not definitely known.

Recently Walden [1] has shown that the value of $d(\gamma s)/dt$ for palmitic and stearic acids is greater than 5 between 60° and 120°. On the basis of the above interpretation of abnormally small values of the temperature coefficient in question, this would appear to indicate that the two acids are highly *dissociated*, whilst direct determinations in solution show that the molecular weights are normal. This affords further evidence in favour of the conclusion indicated above, that the rule of Eötvös is only approximately valid.

The Nature of Surface Tension—A deeper insight into surface tension is obtained on the basis of the molecular theory. We assume that liquid particles attract each other with a force which falls off very rapidly with the distance. A particle in the interior of a liquid is equally attracted on all sides, but a particle in the surface layer is attracted inwards by all the particles of liquid within its sphere of influence, the corresponding attraction by the few particles in the vapour space being negligible in comparison. It follows that at the surface of liquids there is a force—the so-called surface tension—acting inwards, the liquid behaving as if it were covered by an elastic skin.

It is evident that work must be done against molecular attraction in bringing a particle to the surface layer, and therefore the formation of a larger surface involves an expenditure of energy. The surface energy is proportional to the product of the surface tension γ and the area of the surface, and therefore the molecular surface energy is represented by the expression $\gamma(Mv)^{2/3}$, as already mentioned. A liquid tends to diminish the area of its surface as much as possible in virtue of the force tending to draw the particles on the surface towards the interior. The tendency of liquid drops to assume a spherical shape and of minute drops to aggregate to larger drops is thus readily explained. The force of attraction between the molecules in a liquid produces what is known as internal pressure (p. 41),

[1] *Zeitsch. Physikal. Chem.*, 1911, **75**, 555.

which is in many cases of the order of hundreds of atmospheres. Since surface tension is also due to attraction of molecules it affords a rough measure of the internal pressure.

The Parachor—We have seen in the course of this chapter that the measurement of certain physical properties of liquids can be used to throw light on chemical constitution. A further property related to surface tension, and known as *the parachor*, has been used for this purpose by Sugden [1] with considerable success.

Some years ago it was shown by Macleod [2] that the formula

$$\gamma = c(D - d)^4 \quad . \quad . \quad . \quad (1)$$

where γ is the surface tension, D and d are the densities of liquid and saturated vapour respectively and c is a constant, holds over a wide range of temperature. Sugden points out that if the fourth root of Macleod's constant is multiplied by the molecular weight, M, we obtain

$$P = Mc^{1/4} = \frac{M}{D - d} \cdot \gamma^{1/4} \quad . \quad . \quad (2)$$

P being termed *the parachor.*

At low temperatures, when d is small compared with D, $M/(D - d)$ may be taken as the molecular volume of the liquid and we have

$$P = \frac{M}{D}\gamma^{1/4} \quad . \quad . \quad . \quad . \quad (3)$$

It will be evident from formula (3) that the comparison of parachors is equivalent to the comparison of the molecular volumes at temperatures at which liquids have the same surface tension, or, in other words, the same internal pressure.

The magnitude of the parachor, like the molecular refractivity and other properties, depends on the composition and constitution of the molecule and is the sum of two series of constants, one series representing values for the individual atoms, the other values for double and triple bonds, six-membered rings and other factors of constitution. Conversely, from the value

[1] Sugden, *J. Chem. Soc.*, 1924, **125**, 1177, and subsequent papers.
[2] Macleod, *Trans. Faraday Soc.*, 1923, **19**, 38.

of the parachor determined experimentally conclusions can be drawn as to the constitution of the molecule. The parachor is of special interest because it appears to hold consistently for a large number of elements for which the refractrometric and other methods cannot be used.

Practical Illustrations — *Critical Phenomena*—The critical phenomena can be observed in an apparatus, constructed like that of Cagniard la Tour, but more simply as follows: A tube 3-4 mm. internal diameter and 3-4 cm. long is constructed out of a piece of glass tubing, the walls of which are 0·7-0·8 mm. thick, by closing one end in the blow-pipe and drawing out the other at a distance 3-4 cm. from the closed end into a fairly long (5-6 cm.) thick-walled capillary tube. The capillary is then bent, at a point about 1 cm. from the commencement of the wide part of the tube, at right angles to the latter and then partly filled with ether as follows. The tube is warmed and the capillary end dipped into ether, which is drawn into the tube as the latter cools. The ether in the tube is then boiled gently to expel all the air, the end of the capillary dipping all the time in ether, and on again allowing to cool, ether is drawn in so as practically to fill the tube. The excess of ether is then boiled off till the tube is about three-quarters full, the end of the capillary being in ether throughout, and then allowed to cool till the liquid just begins to rise up the capillary tube, showing that the pressure inside is somewhat less than atmospheric; the capillary is then rapidly sealed off near the bend on the side remote from the tube.

In order to observe the capillary phenomena in the tube thus prepared, the latter is suspended by a wire and heated by means of a Bunsen burner held in one hand, the face being protected, in the event of an explosion, by a large plate of glass held in the other hand. In this way, the complete disappearance of the liquid above a certain temperature, and its reappearance on cooling, may be observed without the least danger.

When practicable, the tube may be heated in an iron or copper vessel provided with mica windows, and the critical temperature may be read off on a thermometer placed side by side with the tube in the air bath.

CHAPTER IV

SOLUTIONS

General—Up to the present, we have dealt only with the properties of pure substances which may exist in the gaseous, liquid, or solid state, or simultaneously in two or all of these states. We now proceed to deal with the properties of *mixtures* of two or more pure substances. When these mixtures are homogeneous, they are termed *solutions*.[1] There are various classes of solutions, depending on the state of the components. The more important are :—

(i) Solutions of gases in gases ;
(ii) Solutions of (*a*) gases, (*b*) liquids, (*c*) solids in liquids ;
(iii) Solutions of solids in solids, so-called *solid solutions ;*

and each of these classes will be briefly considered.

A distinction is often drawn between solvent and dissolved substance, but, as will appear particularly from the sections dealing with the mutual solubility of liquids, there is no sharp distinction between the two terms. The component which is present in greater proportion is usually termed the solvent. The dissolved substance is sometimes called the *solute.*

When one of the compounds is present in very small proportion, the system is termed a *dilute solution*, and as the laws representing the behaviour of dilute solutions are comparatively simple, they will be dealt with separately in the next chapter.

Solution of Gases in Gases—This class of solution differs

[1] The term solution is also applied to mixtures which appear homogeneous to the naked eye but heterogeneous when examined with a microscope or ultramicroscope, *e.g.*, colloidal solution of arsenic sulphide.

The usual definition of a solution is " a homogeneous mixture which cannot be separated into its components by mechanical means," but the last part of this definition is open to objection.

from the others in that the components may be present in any proportion, since gases are completely miscible. If no chemical change takes place on mixing two gases, they behave quite independently and the properties of the mixture are therefore the sum of the properties of the constituents. In particular, the total pressure of a mixture of gases is the sum of the pressures which would be exerted by each of the components if it alone occupied the total volume—a law which was discovered by Dalton, and is known as *Dalton's law of partial pressures.* Dalton's law is of the same order of validity as Avogadro's hypothesis; it is nearly true under ordinary conditions, and would in all probability become strictly true at great dilution.

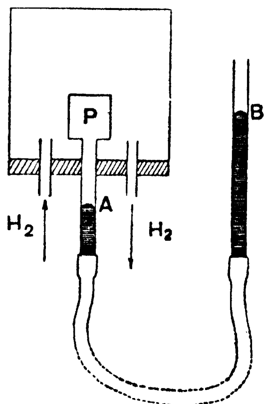


FIG. 12.

Dalton's law can of course be tested by comparing the sum of the pressures exerted separately by two gases with that after admixture, but it is of interest to inquire into the possibility of measuring the partial pressure of one of the components in the mixture itself. It was pointed out by van't Hoff that this is always possible if a membrane can be obtained which allows only one of the gases to pass through. This suggestion was experimentally realized by Ramsay[1] in the case of a mixture of nitrogen and hydrogen as follows: P (Fig. 12) is a palladium vessel containing nitrogen, the pressure of which can be determined from the difference of level between A and B in the manometer, which contains mercury. P is enclosed in another vessel, which can be filled with hydrogen at any desired pressure. The vessel P is heated and a stream of hydrogen at known pressure passed through the outer vessel. As palladium at high temperatures is permeable for hydrogen, but not for nitrogen, the former gas enters P till its pressure outside and inside are equal. The total pressure in P, as measured on the

[1] *Phil. Mag.*, 1894 [v.], **38**, 206.

manometer, is greater than the pressure in the outer vessel, and it is an experimental fact that the excess pressure inside is approximately equal to the partial pressure of the nitrogen.

If, on the other hand, we start with a mixture of hydrogen and nitrogen, and wish to find the partial pressure of the latter, all that is necessary is to put the mixture inside a palladium bulb, keep the latter at a constant high temperature and pass a current of hydrogen at known pressure through the outer vessel till equilibrium is attained, as shown on the manometer. The difference between the external and internal pressure is then the partial pressure of the nitrogen. This very instructive experiment will be referred to later in connection with the modern theory of solutions (p. 109).

Solubility of Gases in Liquids—In contrast to the complete miscibility of gases, liquids are only capable of dissolving gases to a limited extent. When a liquid will not take up any more of a gas at constant temperature it is said to be saturated with the gas, and the resulting solution is termed a *saturated solution*. The amount of a gas taken up by a definite volume of liquid depends on (*a*) the pressure of the gas, (*b*) the temperature, (*c*) the nature of the gas, (*d*) the nature of the liquid.

The greater the pressure of a gas, the greater is the quantity of it taken up by the solvent. For gases which are not very soluble, and do not enter into chemical combination with the solvent, the relation between pressure and solubility is expressed by Henry's law as follows: *The quantity of gas taken up by a given volume of solvent is proportional to the pressure of the gas.* Another way of stating Henry's law is that the *volume* of a gas taken up by a given volume of solvent is independent of the pressure. This is clearly equivalent to the first statement, because when the pressure is doubled the quantity of gas absorbed is doubled, but since its volume, by Boyle's law, is halved, the original and final volumes dissolved are equal.

The question may be regarded from a slightly different point of view, which is instructive in connection with later work. When a definite volume of liquid is saturated with a gas at a certain pressure, there is an equilibrium between the dissolved gas and that over the liquid, and Henry's law may be expressed in the alternative form: *The concentration of the dissolved gas is*

proportional to that in the free space above the liquid. We may consider that the gas distributes itself between the solvent and the free space in a ratio which is independent of the pressure.

For purposes of comparison, the solvent power of a liquid for a gas is best expressed in terms of the "coefficient of solubility," which is the volume of the gas taken up by unit volume of the liquid at a definite temperature.[1] The so-called "absorption coefficient" of Bunsen, in which solubility measurements are still often expressed, is the volume of a gas, reduced to 0° and 76 cm. pressure, which is taken up by unit volume of a liquid at a definite temperature under a gas pressure equal to 76 cm. of mercury. The solubility of gases in liquids diminishes fairly rapidly with rise of temperature.

With regard to the influence of the nature of the gas on the solubility, it may be said in general that gases which have distinct basic or acidic properties, for example, ammonia and hydrogen chloride, are very soluble, whilst neutral gases, such as hydrogen, oxygen, and nitrogen, are comparatively insoluble. Further, gases which are easily liquefied, for example, sulphur dioxide and hydrogen sulphide, are fairly soluble.

As regards the relation between solvent power and the nature of the liquid, very little is known. In general, the order of the solubility of gases in different liquids is the same, and the solvent power of a liquid therefore appears to be to some extent a specific property.

The above remarks are illustrated by the following table, in which the coefficients of solubility of some typical gases in water and in alcohol are given :—

Gas.	Water.	Alcohol.
Ammonia . . .	1050	—
Hydrogen sulphide . .	80	18
Carbon dioxide . .	1·8	4·3
Oxygen . . .	0·04	0·28
Hydrogen . . .	0·02	0·07

[1] Alternatively: the ratio of the concentration in liquid and in gas space.

It may be mentioned that the solubility of gases in water is greatly diminished by the addition of salts, and to a much smaller extent by non-electrolytes. The interpretation of these results has given rise to considerable difference of opinion.

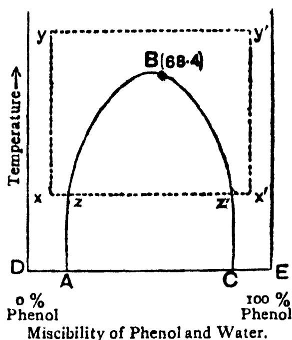
Solubility of Liquids in Liquids—As regards the mutual solubility of liquids, three cases may be distinguished: (1) The liquids mix in all proportions, *e.g.*, alcohol and water; (2) the liquids are practically immiscible, *e.g.*, benzene and water; (3) the liquids are partially miscible, *e.g.*, ether and water.

(1) and (2) *Complete Miscibility and Non-miscibility*—Very little is known as to the factors which determine the miscibility or non-miscibility of liquids. The separation of the components by fractional distillation is discussed in succeeding sections.

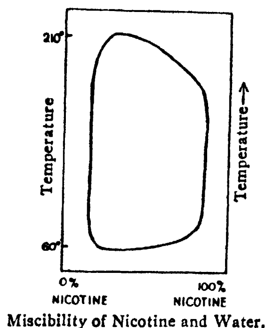
(3) *Partial Miscibility*—If ether, in gradually increasing amounts, is added to water in a separating funnel, and the mixture well shaken after each addition, it will be noticed that at first a homogeneous solution is formed, but when sufficient ether has been added, a separation into two layers takes place on standing. The upper layer is a saturated solution of water in ether, the lower layer a saturated solution of ether in water. As long as the relative quantities of ether and water are such that a separation into two layers takes place on standing, *the composition of these layers is independent of the relative amounts of the components present*, since the composition is determined by the solubility of ether in water and of water in ether at the temperature of experiment. Further, the saturated vapours sent out by the two layers have the same pressure and the same composition—this follows from the fact that they are in equilibrium with the two layers which are in equilibrium with each other.

In the majority of cases, the solubility of two partially miscible liquids increases with the temperature, and it may therefore be anticipated that liquids which in certain proportions form two layers at the ordinary temperature may be completely miscible at higher temperatures. Several such cases are known, for example, phenol and water, which has been investigated by Alexieeff. At room temperature a saturated

solution of phenol in water contains about 8 per cent. of the former component. When more phenol is added two layers are formed and the temperature has to be raised in order to secure complete miscibility. For further additions of phenol up to 36 per cent. the temperature at which complete miscibility occurs rises progressively to 68·4°. In this way the solubility-temperature curve of phenol in water is obtained. Similarly, a saturated solution of water in phenol at 20° contains 28 per cent. of the former component and on further additions of water the temperature of complete miscibility rises progressively to 68·4°, at which point the two solubility-temperature



Miscibility of Phenol and Water.
FIG. 13.



Miscibility of Nicotine and Water.
FIG. 14.

curves meet. These results are represented graphically in Fig. 13, the composition of the mixture being measured on the horizontal axis and temperatures along the vertical axis. The point D represents 0 per cent. phenol (100 per cent. water), E represents 100 per cent. phenol. At all points outside the curve ABC there is complete miscibility, at points inside the curve two layers exist. The maximum represents the temperature, 68·4°, above which phenol and water are miscible in all proportions. If, therefore, we start with a homogeneous solution of phenol in water of the composition represented by the point, x, and gradually add phenol at constant temperature, the composition of the solution will alter along the dotted line xx' until the curve AB is reached at z. This point

represents a saturated solution of phenol in water, and on further addition of phenol a separation into two layers takes place, the compositions of which are represented by the points z and z' respectively. As more phenol is added, the composition of the layers remains unaltered, but the relative amount of the second layer increases until at the point z' only this layer is present, and its composition then alters along zx'. If, however, phenol is added to the same solution at the temperature corresponding with the point y the composition alters along yy' but no separation into two layers takes place. It is evident that there is a striking analogy between the miscibility of two liquids and the critical phenomena represented in Fig. 7. In both cases there is only one phase *outside* the curves AOE and ABC respectively, and two phases at points *inside* the curves. Further, above a certain temperature only one phase can exist in each case, and the temperature of complete miscibility for binary mixtures may therefore be termed the *critical solution temperature.* Moreover, just as we can pass without discontinuity from a gas to a liquid (p. 63), we can pass from a solution containing excess of water to one containing excess of phenol without discontinuity. Starting with a mixture represented by the point x, the temperature is raised above the critical solution temperature along xy, phenol is then added till the point y' is reached and the homogeneous mixture then cooled along $y'x$.

In some cases, however, the solubility of one liquid in another *diminishes* with rise of temperature, thus if a saturated solution of ether in water, prepared at the ordinary temperature, is gently warmed, it becomes turbid, indicating partial separation of the ether. An interesting example of this behaviour is seen in nicotine and water, which are miscible in all proportions at the ordinary temperature, but separate into two layers when the temperature reaches 60°. If a temperature can be reached beyond which the mutual solubility again begins to increase with rise of temperature, the components may again become miscible in all proportions. This has been experimentally realized so far only for nicotine and water, which again become completely miscible when the temperature exceeds 210°. The remarkable solubility relations of these two liquids are therefore

represented by a closed curve (Fig. 14), which will be readily understood by comparison with Fig. 13.

Distillation of Homogeneous Mixtures—A very important matter with reference to binary homogeneous mixtures is the possibility of separating them more or less completely into their components by distillation. Much light is thrown on this question by the investigation of the vapour pressure of the mixture as a function of its composition at constant temperature. Experimental investigation shows that the curve representing the relation between vapour pressure and composition at constant

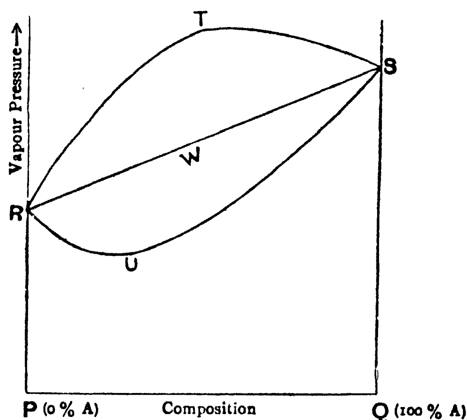


FIG. 15.

temperature usually belongs to one of the three main types, *a*, *b*, and *c* represented in Fig. 15, in which the abscissæ represent the composition of the mixture and the ordinates the corresponding vapour pressures.

(*a*) The vapour-pressure curve of the mixture may have a minimum, as represented by the point U in the curve RUS; example, hydrochloric acid and water. (In the diagram the ordinate PR represents the vapour pressure of B, and QS that of the other pure substance A.

(*b*) The vapour-pressure curve may show a maximum represented by the point T on the curve RTS; example, propyl alcohol and water.

(*c*) The vapour pressure of the binary mixture may lie between those of the pure components A and B, as represented by the curve RWS; example, methyl alcohol and water.

In considering these three typical cases with regard to their bearing on the separation of two liquids by fractional distillation, the important question is the relation between the composition of the boiling liquid and that of the escaping vapour. For a pure liquid, the composition of the escaping vapour is necessarily the same as that of the liquid, but this is not in general the case for a mixture of liquids, and therefore the composition of the mixture may alter continuously during distillation.

Case (*a*). Since a liquid boils when its vapour pressure is equal to the external pressure, it is clear that if a mixture, the vapour-pressure curve of which has a minimum (as in the curve RUS), be boiled, the composition of the liquid will alter in such a way that it tends to approximate to that represented by the point U, since all other mixtures have a higher vapour pressure, and will consequently pass off first. When finally only the mixture U remains, it will distil at constant temperature like a homogeneous liquid, since the composition of the vapour is then the same as that of the liquid. The best-known example of such a constant-boiling liquid is a mixture of hydrochloric acid and water, which boils at 110°. If a mixture containing the components in any other proportion be heated, either hydrochloric acid or water will pass off, and the composition of the liquid will move along the curve to the point of minimum vapour pressure, beyond which it distils as a whole, without further change of composition.

Case (*b*). When, on the other hand, there is a maximum in the vapour-pressure curve, the mixture which has the highest vapour tension will pass over first, and the composition of the residue in the retort will tend towards the component which was present in excess in the initial mixture. In the case of propyl alcohol and water, for example, the mixture which has the highest vapour tension contains from 70 to 80 per cent. alcohol (the maximum being very flat); a mixture of this com position would boil at constant temperature, whilst for one con-

taining more water, some of the latter would finally remain in the retort.

Case (*c*). In this case the composition of the vapour, and therefore the composition of the liquid remaining, alter continuously on distillation. The vapour, and therefore the distillate, will contain the more volatile liquid, A, in greater proportion, and the residue excess of the less volatile liquid, a partial separation being thus effected. If the distillate rich in A is again distilled a mixture still richer in A is at first given off, and the process may be repeated again and again. The more or less complete separation of liquids by this method is termed *fractional distillation.*

It was long thought that constant-boiling mixtures were definite chemical compounds of the two components—for example, HCl, $8H_2O$ in the case of hydrochloric acid and water, but this view was shown by Roscoe to be untenable. He found that the composition of the mixtures does not correspond with simple molecular proportions of the components, and, further, that the composition alters continuously with alteration of the pressure under which the distillation is conducted, which is not likely to be the case if definite chemical compounds are present.

Distillation of Non-Miscible or Partially Miscible Liquids. Steam Distillation—If two immiscible liquids are distilled from the same vessel, since one does not affect the vapour pressure of the other, they will pass over in the ratio of the vapour pressures till one of them is used up. The temperature at which the mixture boils is that at which the *sum* of the vapour pressures is equal to the superincumbent pressure. The curve representing the relation between vapour pressure and composition of the mixture is therefore a straight line (UU′, Fig. 16) parallel to the axis of composition, PU representing the *sum* of the vapour pressures RP and QT, of the two components at the temperature in question.

These considerations are very important in connection with steam distillation. This process is usually employed for the separation of substances with a high boiling-point, such as aniline, and will be familiar to the student. The relative *volumes* of steam and the vapour of the liquid which pass over

are in the ratio of the vapour pressures, p_1 and p_2, at the temperature of the experiment, and the *relative weights* which pass over are therefore in the ratio $p_1d_1 : p_2d_2$, in which d_1 and d_2 are the densities of steam and of the other vapour respectively. Assuming that the system aniline-water boils at 98°, at which temperature the vapour pressure of water is 707 mm. (p_1), the partial pressure of the aniline (p_2) will be 760 — 707 = 53 mm., and the weights of aniline and water which pass over are in the ratio 53 × 93 : 707 × 18 or 4929 : 12,726. This shows that under ideal conditions the ratio of water to aniline in the

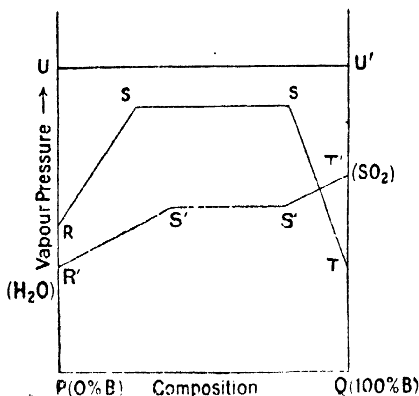


FIG. 16.

distillate is approximately 2·5 : 1, the comparatively small vapour pressure of aniline being partially compensated for by its relatively high molecular weight.

Finally, we consider the distillation from the same vessel of partially miscible liquids. The relation between vapour pressure and composition of the mixture in this case is represented by the curve RSST (Fig. 16), RP representing the vapour pressure of the pure component A, and QT that of the other component B. In general, the vapour pressure of one liquid is lowered by the addition of another. It follows that the vapour pressure of partially miscible liquids, as long as two layers are present, will be represented by a straight line parallel

to the axis of composition, but *lower* than the line UU′ representing the sum of the separate vapour pressures. The pressures when only one phase is present are presented by RS and ST respectively.

In the above type of pressure-concentration curve, the one generally met with in the case of partially miscible liquids, the vapour-pressure curve of the mixture with two liquid phases is greater than that of either compound alone. Another form of curve, represented by R′S′S′T′ (Fig. 16) is illustrated by the system sulphur dioxide-water. On adding sulphur dioxide to water there is an increase in the total vapour pressure, but on adding water to liquid sulphur dioxide the total vapour pressure is diminished.

Solution of Solids in Liquids—In this case the solubility is always limited, and depends on the nature of the solvent and solute and on the temperature. As in the other cases of solubility we are dealing really with an equilibrium, in this case between the dissolved salt and the solid.

Two principal methods are employed for determining the solubility of solids in liquids. (1) Excess of the finely divided solid is shaken continuously with a definite quantity of the solvent at a definite temperature till equilibrium is attained; (2) the solvent is heated with excess of the solute to a temperature higher than that at which the solubility is to be determined, and then cooled to the desired temperature in contact with the solid. The second method is to be recommended when sufficient time is allowed for the attainment of equilibrium at the temperature of experiment, but with suitable precautions the methods give identical results.

It is of interest to note that the solubility depends somewhat upon the state of division of the solids; the more finely divided the solid the greater is the solubility. For fairly soluble salts the difference is negligible, but for slightly soluble salts it may be relatively very considerable. Thus Ostwald has shown that the solubility in water of yellow oxide of mercury is about 14 per cent. greater than that of the coarser-grained red modification.

The results of solubility measurements may be expressed in various ways, for example, as the number of grams of solute

in 100 grams of the solvent, in 100 grams of the solution, or in 100 c.c. of the solution.

When a solution saturated at a high temperature is allowed to cool in the complete absence of the solid solute, the excess of dissolved substance may not separate (*cf.* p. 64), and the solution is then said to be *supersaturated.*

Effect of Change of Temperature on the Solubility of Solids in Liquids—The variation of the solubility in water of certain

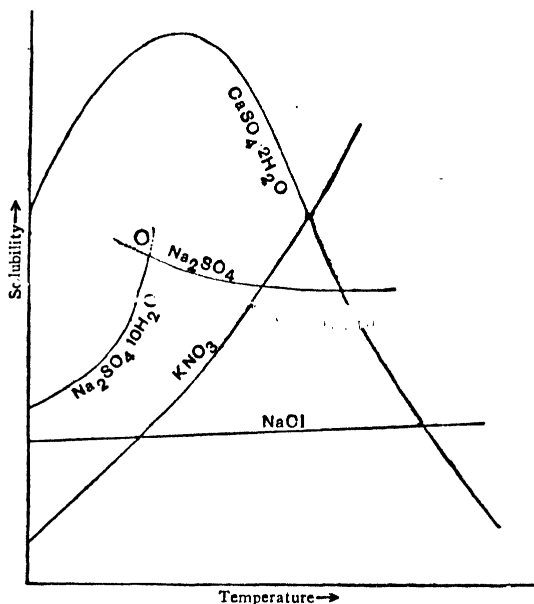


FIG. 17.

salts with change of temperature is shown in Fig. 17, the solubilities being represented as ordinates and the temperatures as abscissæ. The curves are not drawn to scale, but represent diagrammatically the effect of change of temperature.

The solubility of most solids in water increases fairly rapidly with the temperature, *e.g.*, potassium nitrate; but sodium chloride is only slightly more soluble in hot than in cold water. Calcium hydroxide and certain other calcium salts are less

soluble in hot than in cold water; a solution of calcium hydroxide (lime water) saturated at the ordinary temperature, becomes turbid on warming. In the case of calcium sulphate, the solubility increases at first with rise of temperature and then diminishes, so that there is a maximum in the solubility curve as shown in the figure.

Solubility curves are usually continuous, but that representing the solubility of sodium sulphate shows a distinct change of direction at 33°. This is owing to the fact that we are dealing with the solubility curves of two distinct substances. Below 33°, the dissolved salt is in equilibrium with the solid decahydrate Na_2SO_4, $10H_2O$, but the latter splits up into the anhydrous salt and water at 33°, so that the solubility curve at higher temperatures is that of the anhydrous salt. That this explanation of the phenomenon is correct is shown by the fact that the solubility of the anhydrous salt can be determined for a few degrees below 33° in the complete absence of crystals of the decahydrate; the part of the curve thus obtained, represented by the dotted line, is continuous with the right-hand curve.

It is important to remember that *the change to which the break in the solubility curve of sodium sulphate is due takes place in the solid phase and not in the solution.* No well-defined case is known of a sharp break in a curve representing the variation of a physical property in a homogeneous system with temperature or composition.

Relation between Solubility and Chemical Constitution—Very little is known as to causes influencing the mutual solubility of substances and its variation with temperature. In general, it may be said that substances of similar chemical composition are mutually soluble, thus the paraffins are miscible with each other in all proportions, and organic compounds containing the hydroxyl group are all fairly soluble in water. In these cases it does not seem probable that the solubility s connected with anything in the nature of ordinary chemical combination. Phenomena of an apparently different nature are met with in the solubility of gases in liquids, already referred to (p. 95), where it was pointed out that the solvent power is in general a specific property of the solute, and to some extent

independent of the nature of the gas. The solubility of indifferent gases appears in the first instance to depend upon the relative ease with which they can be liquefied.

Solid Solutions[1]—In general, when the temperature of a dilute solution is lowered until partial solidification takes place, the solvent separates in the solid form, practically uncontaminated with the solute. When, however, a solution of iodine in benzene is partially frozen, crystals containing both substances separate, and when solutions of varying concentration are used, there is a constant ratio between the iodine remaining in solution and that in the solidified benzene. This is illustrated in the accompanying table; in the top line is given the concentration C_1 of the iodine in the liquid benzene, in the second line the iodine concentration C_2 in the solid benzene, and in the third line the ratio of the concentrations in solid and liquid, which is approximately constant :—

C_1	3·39	2·587	0·945	per cent.
C_2	1·279	0·925	0·317	,,
C_2/C_1	0·377	0·358	0·336	

This phenomenon exactly corresponds with Henry's law regarding the solubility of gases in liquids (p. 94), and as the crystals containing the two substances are quite homogeneous, they may be regarded as a *solid solution* of iodine in benzene. Similar phenomena have been observed for many other pairs of substances, more particularly for certain metals (p. 201).

Besides crystalline solid solutions, of which an example has just been given, non-crystalline or amorphous solid solutions are known. The hydrogen absorbed by palladium appears to be in solid solution in the metal, but the phenomenon is complicated, and is not yet thoroughly understood. Van't Hoff suggests that two solid solutions are present, hydrogen dissolved in palladium and palladium dissolved in solid hydrogen, corresponding with the two liquid layers formed by phenol and water.

There is evidence that in some cases the dissolved substances can diffuse slowly through the solid solvent, which indicates that the solute exerts osmotic pressure (p. 108).

[1] Compare Bruni, *Feste Losungen und Ismorphismus*, Leipzig, 1908.

Practical Illustrations. (*a*) *Partial Miscibility*—The fact that certain liquids, such as phenol and water, are only partially miscible at ordinary temperatures, but completely miscible above 69°, may be illustrated as follows: 5·6 grams of crystals of phenol are placed in a small separating funnel, and on adding a little water and shaking it will be found that a clear solution is formed, mainly due to the effect of water in lowering the freezing-point of phenol. On further addition of water two layers will be formed, which only disappear when a large excess of water has been added. If, on the other hand, phenol is warmed to 75° in a test tube, and water at the same temperature is gradually added, no separation into two layers will occur, corresponding with the fact that the critical solution temperature has been exceeded.

(*b*) *Solubility and Temperature*—The solubility in water of a salt such as sodium chloride may conveniently be determined as follows. A large test tube is partially filled with distilled water and excess of powdered sodium chloride, and partially immersed in a bath kept at constant temperature. The tube is closed by means of a rubber cork through which passes a glass stirrer, driven by means of a motor. At intervals samples of the solution are removed by means of a pipette, a weighed portion of the solution evaporated to dryness, and the residue weighed. When the concentration of the solution no longer alters, it is saturated. Observations should be made at different temperatures at intervals of 10° and the results plotted on squared paper, the temperatures being plotted as abscissæ, and the solubility expressed as grams of the salt in 100 grams of solvent, as ordinates (Fig. 17).

(*c*) *Supersaturated Solutions*—A supersaturated solution of sodium sulphate may be prepared by heating the salt with half its weight of water in a flask till a perfectly clear solution is obtained; the flask is then plugged with cotton wool and set aside to cool. If a small crystal of the sulphate is added to the cold solution, crystallization at once starts, but crystals not isomorphous with sodium sulphate (*e.g.*, sodium chloride crystals) are not efficient in starting crystallization.

CHAPTER V

DILUTE SOLUTIONS

General—So far, we have dealt in a general way with the properties of solutions, mainly on the lines of the older methods of investigation, as they were practised up to about forty years ago. In 1885, however, a new turn was given to the subject by the enunciation of the modern theory of solution by van't Hoff. Many of the experimental facts on which this theory is based had previously been established by the work of Ostwald, Raoult, and others, and these results were correlated, and many fresh avenues opened for investigation, by van't Hoff's theory, the most important point in which is the conception of *osmotic pressure*, which will now be considered.

It has already been shown that the laws applicable to gases are very simple and that these laws are most strictly followed in the rarefied condition; on the molecular theory this is accounted for by assuming that the particles are then so far apart as to exert little or no mutual influence, and that the space filled by the material of the particles is negligible in comparison with the space occupied. Similarly, we may reasonably anticipate that the laws expressing the behaviour of dissolved substances will be most simple in dilute solution, in other words, when one of the components (the solvent) is present in large proportion compared with the other (the solute), and this is quite borne out by the facts.

Osmotic Pressure. Semi-permeable Membranes—When a few drops of bromine are carefully placed by means of a pipette at the bottom of a jar full of hydrogen or air, and the jar is covered and allowed to stand, it will be found after some time that the heavy bromine vapour has distributed itself uniformly throughout the confined space against the force of gravity.

We may say that the bromine vapour exerts a pressure in virtue of which it diffuses into those parts of the confined space where the pressure is less, and equilibrium is only attained when the pressure is equal throughout. In an exactly similar way, if a sugar solution is carefully covered with a layer of water, the dissolved sugar exerts a pressure with the result that it ultimately becomes uniformly distributed in the solution. This pressure cannot be determined directly, since the external pressure is the sum of this and the pressure of the liquid, but the principle of the method used for measuring it will be understood from its analogy with the method already described for measuring the partial pressure of a gas in a mixture (p. 93). In the latter case, it will always be possible to determine the partial pressure of a gas, A, mixed with another gas, B, when a membrane is known which allows B, but not A, to pass through. Such a membrane is said to be semi-permeable, and for a mixture of nitrogen and hydrogen heated palladium answers the purpose. It is clear that, if we could find a membrane which allows water, but not dissolved sugar, to pass through, the pressure exerted by the latter in solution, its so-called *osmotic pressure*, could be measured.

Such membranes were discovered by Traube, in the course of his experiments on so-called artificial vegetable cells. The most suitable membrane for the purpose was found to be copper ferrocyanide, and the formation of this membrane and its impermeability for certain dissolved salts may be illustrated as follows. A glass tube, provided with a rubber tube and clip at one end and open at the other, is partly filled by suction with an aqueous solution of copper acetate (about 2·8 per cent.) and ammonium sulphate (0·5 per cent.), and the open end, in which the surface of the liquid has been made parallel by adjustment, is then dipped carefully into a 2·4 per cent. aqueous solution of potassium ferrocyanide, containing a little barium chloride, and the tube supported in that position. A thin membrane of copper ferrocyanide forms across the lower end of the tube, and if the experiment has been carefully performed, it will be found that even after standing some hours there is no white precipitate (of barium sulphate) in the lower solution, showing that the membrane is impervious to ammonium

sulphate. Traube tried many other membranes, but none proved so efficient as copper ferrocyanide.

Measurement of Osmotic Pressure—The semi-permeable membranes prepared by Traube were much too weak to withstand fairly large pressures, and their use for actual measurements was only rendered possible by Pfeffer's idea of depositing them in the walls of a porous pot, A (Fig. 18), such as are used for experiments on gas diffusion. The pot is first carefully washed, soaked in water for some time, then nearly filled with a solution of copper sulphate (2·5 grams per litre), dipped nearly to the neck in a solution of potassium ferrocyanide (2·1 grams per litre) and allowed to stand for some hours. The salts diffuse through the walls of the pot and at their junction form a membrane of copper ferrocyanide, which, since it is impermeable for the salts from which it is formed, remains quite thin but is capable of withstanding fairly large pressures, owing to its being supported by the walls. The cell is then taken out, washed, filled with a strong solution of sugar, and closed with a well-fitting rubber cork through which an open glass tube, B, passes. To ensure the tightness of the apparatus, it is of advantage, before forming the membrane, to dip the upper part of the pot, to the depth of about two inches, into melted paraffin, and after the pot is filled and the cork and tube placed in position, the upper surface should be covered with melted paraffin. When a cell thus prepared is placed in water, the water passes in, the pressure inside slowly increases (as shown by the rise in level of the solution in the tube), and finally reaches a point at which, when the cell has been properly prepared, it remains constant for days. The maximum pressure thus attained, in other words, *the excess of pressure which must prevail inside the cell in order to prevent more water flowing in through the semi-permeable membrane*, is termed the *osmotic pressure* of the solution.

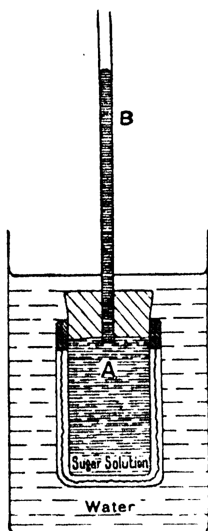


FIG. 18.

In accurate measurements, it is preferable to close the cell with a cork carrying a closed manometer, containing a definite volume of air confined over mercury. Dilution of the solution by the entry of a large volume of water is thus avoided. This arrangement was used by Pfeffer in his original experiments.

The osmotic pressures measured in this way are very considerable—thus a 1 per cent. solution of cane sugar exerts a pressure of more than half an atmosphere, and a 1 per cent. potassium nitrate solution over two atmospheres.

The question as to the relation between osmotic pressure and concentration of the solution was investigated by Pfeffer, and the results obtained for aqueous solutions of sugar and of potassium nitrate at room temperature are given in the accompanying table, in which C represents the concentration of the solution (in grams per 100 c.c. of solution) and P the osmotic pressure (in cm. of mercury).

Cane Sugar.			Potassium Nitrate.		
C	P	P/C	C	P	P/C
1	53·5	53·5	0·8	130·4	163
2	101·6	50·8	1·43	218·5	153
4	208·2	52·1	3·33	436·8	133
6	307·5	51·3			

It is clear from these results that the ratio P/C is approximately constant for any one solution, in other words, the osmotic pressure of a solution is proportional to its concentration. It will be observed that the ratio is somewhat less for potassium nitrate at the higher pressures, a result due in part to the slight permeability of the membrane for the salt under these conditions.

It was also shown by Pfeffer that the osmotic pressure at constant concentration increases with the temperature; some of the results obtained in this connection are quoted on the next page.

The magnitude of the osmotic pressure observed with different membranes was not quite the same, but this must be ascribed to the imperfection of most of the membranes, as it can be shown theoretically that the numerical value of the osmotic pressure is independent of the nature of the membrane, provided the latter is perfectly semi-permeable.

Van't Hoff's Theory of Solutions—Pfeffer's investigations were undertaken for botanical purposes, and their great general importance was only recognized in 1885 by van't Hoff, who used them as the experimental basis of a new theory of solution. We have already seen that osmotic pressure may be regarded as in some respects analogous to gas pressure, and as the former can be measured as described in the previous section we are now in a position, following van't Hoff, to investigate the relationship between osmotic pressure, volume and temperature as has already been done for gases.

As regards the relation between osmotic pressure and volume at constant temperature, we have seen in the previous section that P/C is constant for any one substance, and as the concentration is inversely as the volume in which a definite weight of substance is dissolved, we obtain, by substituting 1/V for C, the equation $PV = \text{constant}$, the exact analogue for solutions of Boyle's law for gases.

With reference to the relation between osmotic pressure and temperature at constant concentration, van't Hoff showed from Pfeffer's observations that *the osmotic pressure*, P, *like the gas pressure*, is proportional to the absolute temperature, T. Some of the observations on which this conclusion is based are given in the accompanying table:—

Cane Sugar.			Sodium Tartrate.		
t	T	P	*t*	T	P
14·2°	287·2	51·0	13·3°	285·3°	90·8
32·0°	305·0	54·4 (54·6)	37·0°	310·0°	98·3 (98·2)

The observed values are given in the third column, with the calculated values in brackets; the agreement is within the limits of experimental error.

From these two equations, $PV = \text{const.}$ and $P \propto T$, we can derive an equation for dilute solutions corresponding to that already obtained for gases (p. 33),

$$PV = rT,$$

in which P represents the osmotic pressure of a solution containing a definite weight of a solute in the volume, V, of solution, and *r* is a constant.

It remains to calculate the numerical value of r for a definite amount, say a mol of a dissolved substance, as has already been done for gases. This can readily be done from Pfeffer's observation that a 1 per cent. solution of cane sugar at 0° exerts an osmotic pressure of 49·3 cm. of mercury. The molecular weight of cane sugar is 342, the volume in which it is contained 34,200 c.c., the pressure is $49{\cdot}3 \times 13{\cdot}59$ gram/cm.^{2}, and the absolute temperature 273°. Hence

$$r = \frac{PV}{T} = \frac{49{\cdot}3 \times 13{\cdot}59 \times 34{,}200}{273} = 83{,}900 \text{ (in gram-cm. units)},$$

a value which almost exactly corresponds with that obtained for gases. As the same value for r is obtained for a mol of other organic compounds, such as urea and glucose, we will represent it by R, to indicate that it is a factor of general importance. We have thus obtained two results of the greatest importance: (1) the equation PV = RT is valid for dilute solutions; (2) the *numerical* value of R is the same for dissolved substances as for gases. The latter statement implies, as is clear from the general equation, that the osmotic pressure of a definite quantity of cane sugar or other substance in solution is equal to the gas pressure which it would exert if it occupied the same volume in the gaseous form. We may therefore say with van't Hoff that "*the osmotic pressure exerted by any substance in solution is the same as it would exert if present as gas in the same volume as that occupied by the solution, provided that the solution is so dilute that the volume occupied by the solute is negligible in comparison with that occupied by the solvent.*" This statement holds for all temperatures, as is at once clear from the fact that the solution obeys the gas laws. Certain important exceptions to the above rule, more particularly in the case of solutions which conduct the electric current, will be discussed in a later chapter.

Some important consequences of the validity of the general equation, PV = RT, for dissolved substances will be dealt with in detail later. In particular, the molecular weight of a dissolved substance is the quantity in grams which, when dissolved in 22·4 litres at 0°, exerts an osmotic pressure of 1 atmosphere, a definition almost exactly analogous to that for gases (p. 42).

The same fact may be expressed somewhat differently as follows: *Quantities of different substances in the ratio of their molecular weights, when dissolved in equal volumes of the same solvent, exert the same osmotic pressure.*

So far, we have considered only the experimental basis of the theory of solution. It has, however, been shown theoretically by van't Hoff, by thermodynamical reasoning, that the osmotic pressure and gas pressure must have the same absolute value, if the solution is sufficiently dilute, and this conclusion has been confirmed by Lord Rayleigh and by Larmor, among others. The latter writer puts the matter as follows: "The change of available energy on further dilution, with which alone we are concerned in the transformations of dilute solutions (*cf.* p. 157), depends only on the further separation of the particles . . . and so is a function only of the number of dissolved molecules per unit volume and of the temperature, and is, per molecule, entirely independent of their constitution and that of the medium,"[1] the assumption being made that the particles are so far apart that their mutual influence is negligible. "The change of available energy" is thus brought into exact correlation with that which occurs in the expansion of a gas.

Recent Direct Measurements of Osmotic Pressure—It is a remarkable fact that, although Pfeffer's osmotic pressure measurements were made as early as 1877, the degree of accuracy attained by him has not been improved upon until recently. Accurate measurements are, however, very desirable, because although the relation between osmotic pressure and concentration can be calculated from the gas laws in dilute solution, there is still much uncertainty as to how far the gas laws are applicable, or what is the exact relationship between osmotic pressure and concentration, in concentrated solutions. In particular, it is, or was until quite recently, uncertain whether V in the general equation, $PV = RT$, should represent the volume of the solvent or that of the solution. This uncertainty has been to some extent removed by the very careful measurements carried out by Morse and Frazer[2] since 1903 by Pfeffer's

[1] Larmor, *Encyc. Britannica*, 10th ed., vol. xxviii., p. 170.

[2] *Amer. Chem. J.*, 1905, **34**, 1; 1906, **36**, 1, 39; 1907, **37**, 324, 425, 558; **38**, 175; 1908, **39**, 667; **40**, 1, 194; 1909, **41**, 1,257; 1911, **45**, 554, etc.

method with slight modifications. Their results show that, if V in the general equation be taken as the volume of the *solvent*, aqueous solutions of cane sugar approximately follow the gas laws up to a concentration of 342 grams of the solute in 1000 grams of water. A few of their results, illustrating the above statement, are given in the accompanying table; the numbers under "gaseous" are calculated on the assumption that the substance as gas occupies the same volume as the *solvent* in the solution.

Concentration of Solution.		Pressure at constant temp. (20°) (atmospheres).		Ratio of osmotic pressure to gas pressure.
Mols per 1000 grams of water.	Mols per litre of solution.	Gaseous.	Osmotic.	
0·10	0·09794	2·39	2·522	1·055
0·20	0·19192	4·78	5·023	1·051
0·40	0·36886	9·56	9·96	1·038
0·60	0·53252	14·34	15·20	1·060
0·80	0·68428	19·12	20·60	1·077
1·00	0·82534	23·90	26·12	1·093

The table shows that only when concentrations are referred to a definite weight (or volume) of *solvent* is there proportionality between concentration and osmotic pressure; if they are referred to a constant volume of *solution* (column 2) the osmotic pressure increases faster than the concentration. The numbers in the fifth column show, however, that the osmotic pressure at 20° is on the average about 6 per cent. greater than the gas pressure. Curiously enough, the ratio is about the same at all temperatures from 0° to 25°.

Another direct method of measuring osmotic pressure based on an entirely different principle was used by the Earl of Berkeley and E. G. Hartley. Instead of measuring the pressure produced in a cell by the passage inwards of solvent, they subjected the solution, separated from the solvent by a semi-permeable membrane, to a pressure which is just sufficient to prevent the inflow of solvent. This balancing pressure is taken as the osmotic pressure. By this method Berkeley and Hartley measured pressures up to 130 atmospheres.

Other Methods of Determining Osmotic Pressure—The difficulties inherent in the direct determination of osmotic pressure

can often be avoided by determining it indirectly by comparison with a solution of known osmotic pressure. Solutions which have the same osmotic pressure are said to be *isotonic* or *isosmotic*.

One such method, used by de Vries,[1] depends on the use of plant cells as semi-permeable membranes. The protoplasmic layer which surrounds the cell-sap is permeable to water, but impermeable to many substances dissolved in the cell-sap, such as glucose and potassium malate. If such a cell is placed in contact with a solution of higher osmotic pressure than the cell-sap, water is withdrawn from the cell (just as a sugar solution absorbs water through a semi-permeable membrane) and the protoplasm shrinks away from the cell-wall; a phenomenon which is termed *plasmolysis*. If, however, the solution has a smaller osmotic pressure than that of the cell-sap, water enters the cell, the protoplasm expands and lines the cell-wall. The behaviour of the protoplasm, especially if coloured, can be followed under the microscope, and by trial a solution can be found which has comparatively little effect upon the appearance of the cell, and is therefore isotonic with the cell contents.

A method depending on the same principle, in which red blood corpuscles are used instead of vegetable cells, has been described by Hamburger,[2] and the cell-walls of bacteria may also be used as semi-permeable membranes.

The following table contains some "isotonic coefficients" as given by de Vries and by Hamburger; the numbers represent the ratio of the osmotic pressures of *equimolecular* or equimolar solutions of the compounds mentioned.

Substance.	Isotonic Coefficients. Plasmolytic Method.	With Red Blood Corpuscles.
Cane sugar	1·81	1·72
Potassium nitrate	3·0	3·0
Sodium chloride	3·0	3·0
Calcium chloride	4·33	4·05

It will be observed that, although the results obtained by the two methods agree fairly well, the osmotic pressures for equi-

[1] *Zeitsch. physikal. Chem.*, 1888, **2**, 415.
[2] *Ibid.*, 1890, **6**, 319.

valent solutions are not equal, as would be expected according to Avogadro's hypothesis. The deviation from the expected result is such that potassium nitrate, for example, exerts an osmotic pressure about 1·7 times greater than that due to an equimolar solution of cane sugar. This observation is of fundamental importance in connection with modern views as to salt solutions.

The Mechanism of Osmotic Pressure—The foregoing considerations are quite independent of any hypothesis as to the exact nature of osmotic pressure, and so far no general agreement has been reached on this point. Van't Hoff inclines to the view that the pressure is to be accounted for on kinetic grounds,[1] perhaps as being due to the bombardment of the walls of the vessel by solute particles, in the same way as the pressure of a gas is produced according to the kinetic theory, and the fact that the osmotic pressure is proportional to the absolute temperature appears rather to support this suggestion. Other views are that it is connected with attraction between solvent and solute, or perhaps with surface tension effects. It may be pointed out that the equivalence of osmotic pressure and gas pressure in great dilution is no evidence that they arise from the same cause.

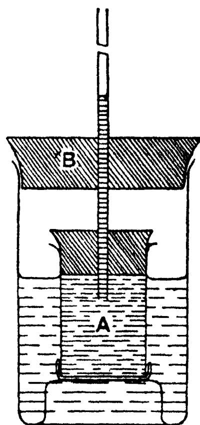


FIG. 19.

As regards semi-permeable membranes, their efficiency does not depend, as might at first be supposed, on anything in the nature of a sieve action, only the smaller molecules being allowed to pass, but rather upon a difference in their solvent power for the two components of the mixture. The action of the palladium in Ramsay's experiment (p. 93) is very probably to be accounted for in this way, and that the same is true for solutions is well illustrated by an instructive experiment due to Nernst and illustrated in Fig. 19. The wide cylindrical glass tube, A, is

[1] For a discussion between van't Hoff and Lothar Meyer on this point, see *Zeitsch physikal. Chem.*, 1890, **5**, 23, 174.

closed at the bottom with an animal membrane (bladder) which has previously been thoroughly soaked in water; it is then filled with a mixture of ether and benzene and fitted with a cork and narrow tube, as shown in the figure. The cell is supported on a piece of wire gauze in a beaker partly filled with moist ether and loosely closed by a cork, B. After a time it will be observed that the liquid has risen to a considerable height in the narrow tube. What occurs in this case is that the ether dissolves in the water with which the membrane is soaked, and in this way is transferred inside the cell, whilst the benzene, being insoluble in water, is unable to pass out. Similarly, the efficiency of the copper ferrocyanide membrane may depend on its solvent power for water but not for sugar.

Osmotic Pressure and Diffusion—It has already been pointed out that there is a close connection between osmotic pressure, as defined above, and diffusion; it is the difference in the osmotic pressure of cane sugar in different parts of a system which causes it in time to be uniformly distributed through that system. The diffusion of dissolved substances was very fully investigated by Graham, but the general law of diffusion was first enunciated by Fick. Fick's law is comprised in the equation

$$ds = -\,DA\frac{dc}{dx}dt,$$

which states that the amount of solute, ds, which passes through the cross-section of a diffusion cylinder is proportional to the area, A, of the cross-section, to the difference of concentration, dc, at two points at a distance, dx, from one another, to the time, dt, and to a constant, D, characteristic for the substance, and termed the *diffusion-constant*. As an illustration of the above formula, it was found that when $dc = 1$ gram per c.c., $dx = 1$ cm., $A = 1$ sq. cm. and $dt =$ one day, that 0·75 gram of sodium chloride passed between the two surfaces. This is excessively slow, in comparison with the high osmotic pressures set up even by dilute solutions, and the explanation is to be found in the great friction due to the smallness of the particles. As the driving force—the osmotic pressure—and the rate of diffusion are known, the resistance to the movement of the particles can

be obtained. It has been calculated that the enormous force of four million tons weight is needed to force 1 gram mol of cane sugar through water at a velocity of 1 cm. per sec. The more rapid diffusion in gases may plausibly be ascribed to the much smaller resistance to the movement of the particles.

The rate of diffusion is much influenced by temperature and, curiously enough, to about the same extent for all solutes the average increase is about $\frac{1}{40}$ of the value at 18° for every degree C.

MOLECULAR WEIGHT OF DISSOLVED SUBSTANCES

General—It has already been pointed out (p. 113) that since Avogadro's hypothesis is valid for solutions, the molecular weight of a dissolved substance can readily be calculated when the osmotic pressure exerted by a solution of known concentration at known temperature and pressure is known. An illustration of this is given on the next page. As, however, the direct measurement of osmotic pressure is a matter of considerable difficulty, it has been found more convenient for the purpose to measure other properties of solutions, *the relationship of which to the osmotic pressure is known.* The only three methods which can be dealt with here are :—

(1) The lowering of vapour pressure ;
(2) The elevation of boiling-point ;
(3) The lowering of freezing-point,

brought about by adding a known weight of solute to a known weight or volume of solvent.

It can be shown by thermodynamical reasoning (p. 136) that under certain conditions the lowering of vapour pressure, the elevation of the boiling-point and the lowering of the freezing-point due to the addition of a definite quantity of solute to a definite volume of solvent are each proportional to the osmotic pressure of the solution. Further, the equations expressing the exact relationships between these three factors and the osmotic pressure have also been established,[1] and all these theoretical deductions have been fully confirmed by experiment. *It follows that just as equimolecular quantities of different substances in*

[1] Appendix, pp. 136-142.

equal volumes of the same solvent exert the same osmotic pressure, so equimolecular quantities of different substances in equal volumes of the same solvent raise the boiling-point, lower the freezing-point, and lower the vapour tension to the same extent. These statements find a very simple representation on the molecular theory. Since equimolecular quantities of different substances contain the same number of molecules, it follows that the magnitude of the osmotic pressure, lowering of vapour pressure, etc., depends only on the *number* of particles present and is independent of their nature (colligative properties, p. 72).

The molecular weight of the solute could, of course, be obtained by determining one of the factors (1), (2), (3) and then calculating the value of the osmotic pressure, but it is much simpler to obtain the molecular weight by comparison with a substance of known molecular weight.

It may be mentioned that besides the methods just indicated, there are other analogous methods for determining molecular weights which, from considerations of space, cannot be referred to here. Nernst has pointed out that any process involving the separation of solvent and solute can be used for determining molecular weights, and a little consideration will show that the four methods just mentioned come under this heading. Moreover, the osmotic effect of the solute is to diminish the readiness with which part of the solvent may be separated from the solution, and the work done in removing a volume of solvent, v, from the solution is proportional to the osmotic pressure. The effect of the solute on the boiling- and freezing-points of the solvent must therefore be in the direction already indicated. The mathematical proof of the connection between these four properties depends upon the equivalence of the work done in removing part of the solvent from the solution by different methods (Appendix).

The four different methods for determining molecular weights in solution and the general nature of the results obtained will now be considered in detail.

Molecular Weights from Osmotic Pressure Measurements. (*a*) *From absolute values of the osmotic pressure*—The principle of this method has already been discussed (p. 113). If g grams of substance, dissolved in v c.c. of solvent, gives an osmotic

pressure of p cm. at T° abs., the molecular weight, m, will be that quantity which, when present in 22,400 c.c. of solvent, will give an osmotic pressure of 76 cm. Hence, since pv/T is proportional to the amount of substance used (p. 33),

$$g : \frac{pv}{273 + t} :: m :: \frac{22{,}400 \times 76}{273},$$

$$\text{or } m = \frac{g \times 22{,}400 \times 76 \times (273 + t^\circ)}{273pv}.$$

As an example, we will take an experiment of Morse and Frazer (p. 114) in which a solution containing 34·2 grams of sugar in 1000 c.c. (really 1000 grams) of water gave an osmotic pressure of 2·522 atmospheres = 191·6 cm. at 20°. Hence

$$m = \frac{34{\cdot}2 \times 22{,}400 \times 76 \times 293}{273 \times 191{\cdot}6 \times 1000} = 326{\cdot}0$$

as compared with the theoretical value of 342.

Alternatively, by formula (2), p. 43,

$$m = \frac{gRT}{pv} = \frac{342 \times 0{\cdot}08205 \times 293}{2{\cdot}522 \times 1} = 326.$$

(*b*) *By comparison of osmotic pressures*—Since equimolecular solutions in the same solvent have the same osmotic pressure, it is only necessary to find the strengths of two solutions which are in osmotic equilibrium (isotonic), and if the molecular weight of one solute is known that of the other can be calculated. De Vries found that a 3·42 per cent. solution of cane sugar was isotonic with a 5·96 per cent. solution of raffinose, the molecular weight of which was then unknown. If it be represented by x, then 3·42 : 5·96 : : 342 : : x, whence $x = 596$. This result has since been confirmed by chemical methods.

Lowering of Vapour Pressure—It has long been known that the vapour pressure of a liquid is diminished when a non-volatile substance is dissolved in it, and that the diminution is proportional to the amount of solute added. In 1848 von Babo showed that the relative lowering of vapour pressure (*i.e.*, the ratio of the observed lowering and the original pressure) is independent of the temperature. In 1887 Raoult, on the basis of a large amount of experimental work, established the following important rule: *Equimolecular quantities of different substances, dissolved in equal volumes of the same solvent, lower*

the vapour pressure to the same extent. On comparing the relative lowering in different solvents, the same observer discovered another important rule, which may be expressed as follows: *The relative lowering of vapour pressure is equal to the ratio of the number of molecules of solute and the total number of molecules in the solution.* Putting p_1 and p_2 for the vapour pressures of solvent and solution respectively, the rule may be put in the form

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N + n}$$

in which n and N represent the number of molecules of solute and solvent respectively. In order to illustrate the validity of this rule, some results given by Raoult are quoted in the accompanying table; the relative lowering is that due to the addition of 1 mol of solute to 100 mols of the various solvents:—

Solvent.	H_2O	PCl_3	CS_2	CCl_4	CH_3I	$(C_2H_5)_2O$	CH_3OH
Relative lowering	0·0102	0·0108	0·0105	0·0105	0·0105	0·0096	0·0103

The results agree excellently among themselves, and fairly well with the calculated value, $1/101 = 0·0099$.

About the same time van't Hoff introduced the conception of osmotic pressure, and showed by a thermodynamical method (p. 136) that the relation between the relative lowering of vapour pressure and the osmotic pressure is given by the equation

$$\frac{p_1 - p_2}{p_1} = \frac{M}{sRT} . P \quad . \quad . \quad . \quad (1)$$

where M = molecular weight of solvent, *in the form of vapour*, s is its density, and the other symbols have their usual significance. The expression M/sRT is therefore constant, since it depends only on the nature of the solvent, and consequently the relative lowering of vapour pressure is proportional to the osmotic pressure, P. By using the general equation, $PV = nRT$ (where n is the number of mols of solute), P in equation (1) can be eliminated,[1] and we finally obtain

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N}.$$

[1] $P = \frac{nRT}{V}$, where V is the volume of the solvent. If N represents the number of mols of solvent, M its molecular weight and s its density,

This equation differs from that of Raoult in that the denominator on the right-hand side is N instead of $N + n$, but they become identical "at infinite dilution" when the volume of the solute is negligible in comparison with that of the solvent.

By substituting g/m for n and W/M for N, where g and W are the weights of solute and solvent respectively, m is the (unknown) molecular weight of the solute and M that of the solvent in the form of vapour, we obtain the equation

$$\frac{p_1 - p_2}{p_1} = \frac{gM}{Wm},$$

which enables us to calculate the molecular weight of a dissolved substance when the relative lowering produced by a known weight of solute in a known weight of solvent is known. As an illustration, an experiment of Smits may be quoted. He found that at 0° the lowering of vapour pressure produced by adding 29·0358 grams of sugar to 1000 grams of water is 0·00705 mm., the vapour pressure of water at that temperature being 4·62 mm. Hence

$$\frac{0{\cdot}00705}{4{\cdot}62} = \frac{29{\cdot}0358 \times 18}{1000m}, \text{ and } m = 342,$$

in exact agreement with the theoretical value.

As the lowering of vapour pressure is very small and not very easy to determine accurately by a statical method, it has not been very largely used for molecular weight determinations, the closely allied method depending on the elevation of the boiling-point being preferred. It has, however, one great advantage, inasmuch as, unlike the boiling-point and freezing-point methods, it can be used for the same solution at widely different temperatures. For this purpose, a dynamical method suggested by Ostwald and worked out by Walker[1] has certain advantages. A current of air is drawn in succession through (1) a set of Liebig's bulbs containing the solution of vapour pressure p_2, (2) similar bulbs containing the pure solvent vapour

the volume V of the solvent = MN/s. Hence $P = \frac{nRTs}{MN}$, and when this value is substituted in equation (1) we obtain $(p_1 - p_2)/p_1 = n/N$.

[1] *Zeitsch. physikal. Chem.*, 1888, **2**, 602.

pressure p_1, (3) a U-tube containing concentrated sulphuric acid. In the first set of bulbs it becomes saturated up to p_2 with the vapour of the solvent, in the second set up to p_1, in the U-tube the moisture is completely absorbed. The loss of weight in the second set of bulbs is proportional to $p_1 - p_2$, and the gain in the U-tube to p_1 (*cf.* p. 102).[1]

Elevation of Boiling-point—A little consideration shows that there is a close connection between this method of determining molecular weights and that depending on the lowering of vapour pressure. A liquid boils when its vapour pressure is equal to that of the atmosphere. The presence of a solute lowers the vapour pressure, and to reach the same pressure as before we require to raise the temperature a little; it is evident that, to a first approximation, this elevation must be proportional to the lowering of vapour pressure. It follows that, in this case also, equimolecular quantities of different solutes, in equal volumes of the same solvent, raise the boiling-point to the same extent. The molecular weight of any soluble substance may therefore be found by comparing its effect on the boiling-point of a solvent with that of a substance of known molecular weight.

For this purpose, it is convenient to determine the *molecular elevation constant*, K, for each solvent, that is, the elevation of boiling-point which would be produced by dissolving a mol of any substance in 100 grams or 100 c.c. of the solvent. Actually, of course, the elevation is determined in fairly dilute solution, and the value of the constant calculated on the assumption that the rise of boiling-point is proportional to the concentration. Then the weight in grams of any other compound which, when dissolved in 100 grams or 100 c.c. of the solvent, produces a rise of K degrees in the boiling-point is the molecular weight.

If g grams of substance, of unknown molecular weight, m, dissolved in L grams of solvent raises the boiling-point δ degrees, whilst m grams in 100 grams of solvent give a rise of K degrees, it follows, since $100g/L$ is the number of grams of substance in 100 grams of solvent, that

[1] A modification of this method has been used by Lord Berkeley and Hartley for the indirect determination of the osmotic pressure of concentrated solutions of cane sugar (*Proc. Roy. Soc.*, 1906, 77A, 156).

$$\frac{100g}{L} : \delta :: m :: K, \text{ whence } m = \frac{100gK}{L\delta}.$$

In the course of the last few years, the constants for 100 grams and 100 c.c. have been very carefully determined for a large number of solvents, and some of the more important data are given in the accompanying table :—

Solvent.	Molecular Elevation Constant.	
	100 grams.	100 c.c.
Water	5·2	5·4
Alcohol	11·5	15·6
Ether	21·0	30·3
Acetone	16·7	22·2
Benzene	26·7	32·8
Chloroform	39·0	27·7

Van't Hoff has shown (p. 141) that these constants, some of which had previously been obtained empirically by Raoult, can be calculated from the latent heat of vaporization, H, per gram of solvent, and its boiling-point, T, on the absolute scale, by means of the formula

$$K = \frac{0{\cdot}02T^2}{H}.$$

As an example, the calculated value for the molecular elevation constant for water, the latent heat of evaporization of which at its boiling-point is 537 calories, is

$$K = (0{\cdot}02 \times (373)^2)/537 = 5{\cdot}2$$

in satisfactory agreement with the experimental value. For all solvents which have been carefully investigated, the experimental and calculated values are in good agreement.[1]

Experimental Determination of Molecular Weights by the Boiling-point Method—The ease and certainty with which such determinations can now be made is largely due to the work of Beckmann. One of the methods suggested by him will first be considered, and then a method due to Landsberger, based on a different principle.

[1] The observed and calculated values for a large number of solvents are given in Landolt and Börnstein's tables.

(*a*) *Beckmann's Method*—The apparatus used is represented in Fig. 20. The boiling-tube, A, is provided with two side

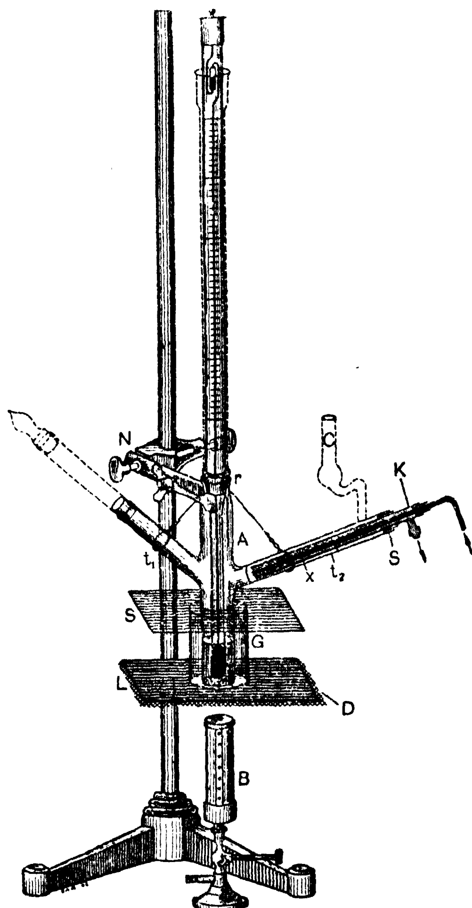


FIG. 20.

tubes, t_1, by means of which the solute (solid or liquid) is introduced, and t_2, which is connected to a small condenser, by the action of which the amount of solvent is kept fairly

constant. The solution is made to boil by the heat from a small screened burner, B, which can be carefully regulated, and the boiling liquid is insulated by means of an air jacket between the outer cylindrical glass tube, G, and the boiling tube. As the temperature of the vapour which escapes from a boiling solution is little, if any, above the boiling-point of the pure solvent, it is necessary to place the thermometer in the boiling liquid so that the bulb is completely immersed. The liquid tends to become superheated, and to eliminate this source of error Beckmann recommends filling up the boiling-tube nearly to the level of the liquid with glass beads or garnets, or, still better, with platinum tetrahedra. The thermometer represented in the figure, which was specially designed by Beckmann for this work, has a large bulb and an open scale, covering only 5°-6°, and graduated in $\frac{1}{100}$°. To render the thermometer available for widely different temperatures, there is an arrangement by means of which the amount of mercury in the bulb can be so adjusted that the top of the thread can be brought on the scale at any desired temperature. The solvent, of which 10 to 15 grams is usually sufficient, is measured with a pipette, or weighed by difference in the boiling-tube itself; the solute, if solid, may be conveniently introduced in the form of a compressed pastille or, if liquid, by means of a bent pipette. The boiling-point of the solvent is determined by causing it to boil fairly vigorously, and the temperature should remain constant within 0·01°-0·015° for about twenty minutes while readings are being taken. The temperature is then allowed to fall several degrees by removing the source of heat, the solute rapidly introduced, the boiling-point again determined, a fresh quantity of solute introduced, the boiling-point re-determined, and so on. The thermometer should be tapped before each reading. The amount of solute added may conveniently be such that the boiling-point is raised 0·15°-0·2° after each addition. It may be pointed out that more satisfactory results are usually obtained when differences produced by the addition of more solute are used in the calculation than when differences in the boiling-point of solvent and solution are used.

As an illustration of the calculation of the results, an experiment with camphor in ethyl alcohol may be quoted. The

addition of 0·56 gram of camphor to 16 grams of the solvent raised its boiling-point 0·278°. Hence

$$m = \frac{100gK}{L\delta} = \frac{100 \times 0{\cdot}56 \times 11{\cdot}5}{16 \times 0{\cdot}278} = 145$$

the theoretical value for $C_{10}H_{16}O$ being 142.

With proper precautions, the results obtained by this method are accurate within 3-4 per cent.

(*b*) *Landsberger's Method*—This method depends upon the fact that a solution can be heated to its boiling-point by passing into it a stream of the vapour of the boiling solvent. In this case there is little or no risk of superheating, as the temperature of the vapour is *lower* than the boiling-point of the solution. The boiling-point of the solvent is first determined by passing in vapour till the temperature ceases to rise, some of the solute is then added, and more vapour passed in until the boiling-point of the solution is reached. As, during the heating, the amount of solvent increases by condensation of vapour, the final amount of solution, upon which of course the observed boiling-point depends, is obtained by weighing after the experiment. If no great accuracy is required, the final volume may be read off in the boiling-tube, graduated for the purpose. Radiation may be minimised by jacketing the inner tube with the vapour of the boiling solvent.

Depression of the Freezing-point—This is the most accurate and most largely employed method for the determination of molecular weights in solution. The two necessary conditions for its applicability are (1) the pure solvent, free from any of the solute, must separate out when the freezing-point is reached; (2) only a little of the solvent must have separated when the measurement is taken, otherwise the concentration of the solution will be appreciably altered. As in solubility determinations, we are dealing with an equilibrium (p. 103) in this case between ice and solution, and the experimental fact is that *the more concentrated the solution the lower is the temperature at which equilibrium is reached.* It is thus evident that if a large amount of the solvent separates in the solid form, the observed freezing-point is the temperature of equilibrium with a more concentrated solution than that originally prepared.

In this case also, the osmotic pressure, and hence the molecular weight, could be calculated from the formula connecting osmotic pressure and depression of the freezing-point (p. 144), but the comparison method is always used. Just as for the boiling-point (p. 124) the *molecular freezing-point depression*, *i.e.*, the depression produced by dissolving 1 mol of solute in 100 grams or 100 c.c. of the solvent, has been determined for a large number of solvents, and some of the more important data are given in the accompanying table:—

Solvent.	Molecular Depression. 100 grams.	100 c.c.
Water	18·5	18·5
Benzol	50	56
Acetic acid	39	41
Phenol	74	—
Naphthalene	69	—

The molecular depression, K, can be calculated from the latent heat of fusion, H, of the solvent and its freezing-point on the absolute scale by means of the expression

$$K = \frac{0{\cdot}02T^2}{H}$$

analogous to that which holds for the boiling-point elevation. Thus for water we have $K = (0{\cdot}02 \times (273)^2)/80 = 18{\cdot}6$.

It may be mentioned, as a matter of historical interest, that the experimental values for K obtained with solutions of cane sugar by Raoult, Jones, and others, were at first much greater than 18·6, but the careful experiments of Abegg, Loomis, Wildermann, and later of Raoult himself, made it clear that the high values previously obtained were due to experimental error, and that, with proper precautions, the value of K deduced on the basis of the theory of solution was fully confirmed by experiment.

If g grams of solute, in L grams of solvent, caused a depression, Δ, of the freezing-point of the solvent, the molecular weight of the solute can be calculated from the formula

$$M = \frac{100gK}{\Delta L},$$

which exactly corresponds with that already given for elevation of boiling-point.

Experimental Determination of Molecular Weights by the Freezing-point Method—The apparatus which is used almost exclusively for this purpose was also designed by Beckmann, and is shown in Fig. 21. The inner tube, A, which contains the solvent, has a side tube by which the solute may be introduced, and is provided with a Beckmann thermometer, D, and a stirrer, preferably of platinum. The remainder of the apparatus consists of a tube, B, rather wider than A, and fitted into the loose cover of the large beaker, C, which contains water or a freezing-mixture (ice, or ice and salt), the temperature of which is 2°-3° below the freezing-point of the solvent.

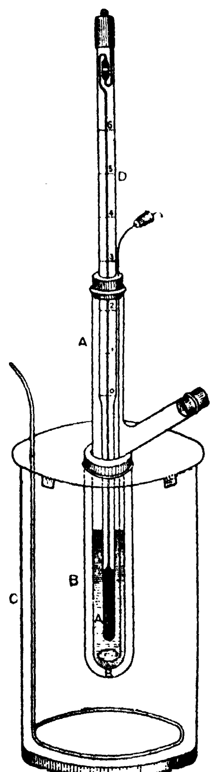


Fig. 21.

In making an experiment, 15-20 grams of the solvent are weighed or measured into the tube, A, the stirrer and thermometer are put in place, and A is then placed in the wider tube B, which acts as an air mantle. The liquid is then stirred continuously and the thermometer observed. Owing to supercooling, the temperature falls below the freezing-point of the solvent, but as soon as solid begins to separate, it rises rapidly, owing to the latent heat set free, and the highest temperature observed is taken as the freezing-point of the solvent. The tube is then removed from the bath, the solid allowed to melt, a weighed amount of the solute added, and the determination of the freezing-point repeated. A further portion of solute may then be added, and another reading taken. With some solvents there is considerable supercooling, and as this would be a source of error owing to separation of much solvent when solidification finally occurs, a small particle of solid sol-

vent is added to start solidification when the temperature has fallen 1°-2° below the freezing-point.

As an illustration of the calculation of the results, an experiment with naphthalene in benzene may be quoted. The addition of 0·142 gram of the compound to 20·25 grams of the solvent lowered the freezing-point 0·284°. Hence

$$m = \frac{100gK}{\Delta L} \quad \frac{100 \times 0{\cdot}142 \times 51{\cdot}2}{0{\cdot}284 \times 20{\cdot}25} = 126$$

as compared with the theoretical value 128.

Results of Molecular Weight Determinations in Solution. General—The most important result of the numerous molecular weight determinations of dissolved substances which have been made in recent years is that in general *the molecular weight in dilute solution is the same as that deduced from the simple chemical formula of the solute, as based on vapour density determinations or on its chemical behaviour.* For example, the empirical formula of naphthalene is C_5H_4, and since one-eighth of the hydrogen can be replaced, the simplest chemical formula must be $C_{10}H_8$, and the molecular weight 128. Cryoscopic determinations in benzene gave a value 126, so that naphthalene is present as simple molecules in solution.

The van't Hoff-Raoult formulæ (p. 122) on which the determination of molecular weights in solution depend, have been deduced on certain assumptions which hold only for dilute solutions, and it is of the utmost importance to bear in mind that there is no *a priori* reason why they should give trustworthy results for concentrated solutions. The question as to how far the gas laws hold for concentrated solution, or what modifications are necessary, has been much debated, but so far no definite conclusions have been arrived at. It is mainly a matter for further experiment. It has already been shown (p. 115) that when V in the general formula is taken as the volume of the solvent, the normal molecular weight is obtained for cane sugar up to very high concentrations on the assumption that the gas laws are valid for these solutions. The same is true for other compounds, more particularly in organic solvents,

as may be illustrated by the values obtained by Beckmann for camphor in benzene [1] (theoretical value 152):—

Concentration.	Value of *m*.	Concentration.	Value of *m*.
0·411	144	12·11	149
1·253	143	23·12	152
2·791	145	26·59	154
5·897	147		

The observed molecular weights depend not only on the nature of the solute and on the concentration, but also very largely on the nature of the solvent. Examples will be given in the following pages showing that in certain solvents the observed molecular weights are often higher than those deduced from the chemical formula of the solute. The solute is then said to form complex molecules or to be *associated*, and the solvent is termed an *associating* solvent. In other solvents, on the contrary, the molecular weight may be equal to or less than that deduced from its chemical formula. In the latter case the solute is said to be *dissociated*, and the solvents in question are termed *dissociating* solvents.

Abnormal Molecular Weights—In order to illustrate the results of molecular weight determinations from a slightly different point of view, the following table contains the values for the molecular freezing-point depression, K, for three typical solvents, water, acetic acid, and benzene. The data are mainly due to Raoult, and in calculating K it is assumed that the molecular weight corresponds with the ordinary chemical formula of the solute:—

Solvent—Water.		Solvent—Acetic Acid.		Solvent—Benzene.	
Solute.	K.	Solute.	K.	Solute.	K.
Cane sugar	18·6	Methyl iodide	38·8	Methyl iodide	50·4
Acetone	17·1	Ether	39·4	Ether	49·7
Glycerol	17·1	Acetone	38·1	Acetone	49·3
Urea	18·7	Methyl alcohol	35·7	Aniline	46·3
HCl	39·1	HCl	17·2	Methyl alcohol	25·3
HNO_3	35·8	H_2SO_4	18·6	Phenol	32·4
KNO_3	35·8	$(CH_3COO)_2Mg$	18·2	Acetic acid	25·3
NaCl	36·0			Benzoic acid	25·4

[1] Concentration in grams per 100 grams of benzene.

This very instructive table shows that, for all three solvents, there are two sets of values for K, one of which is approximately double the other. The question now arises as to which of these are the normal values, obtained when the solute exists as single molecules in solution. This can at once be settled by using van't Hoff's formula, $K = (0{\cdot}02T^2)/H$ (p. 125), and we find that the normal depressions are 18·6, 39·0, and 51·2 for water, acetic acid, and benzene respectively. This means that acetic acid, phenol and some other compounds dissolved in benzene produce only half the depression, in other words, exert only about half the osmotic pressure that would be expected according to their formulæ, whilst in water certain acids and salts have an abnormally high osmotic pressure. The osmotic pressure of certain mineral acids in acetic acid is abnormally low.

On the molecular theory, an abnormally small osmotic pressure shows that the number of particles is smaller than was anticipated. The experimental results can be satisfactorily accounted for on the view that acetic acid and benzoic acid exist as double molecules in benzene solution, and that phenol is polymerized to a somewhat smaller extent. This explanation seems the more plausible inasmuch as acetic acid contains complex molecules in the form of vapour (p. 47).

It is mainly compounds containing the hydroxyl and cyanogen groups which are polymerized in non-dissociating solvents; in dissociating solvents, such as water and acetic acid,[1] these compounds have normal molecular weights.

It may be anticipated that the molecular complexity of solutes will be greater in concentrated solutions, and the available data appear to show that such is the case. The results are, however, somewhat uncertain, inasmuch as in concentrated solution the gas laws are no longer valid (p. 131).

Solvents such as benzene are sometimes termed associating solvents, but this probably does not mean that they exert any associating effect. There is a good deal of evidence to show that the substances existing as complex molecules in benzene and chloroform solution are complex in the free condition, and

[1] That acetic acid is in some cases at least a dissociating solvent is evident from the fact that the molecular weight of methyl alcohol in it is almost normal.

that the complex molecules are only partly broken up in so-called associating solvents.

The explanation of the behaviour of solutes in water is by no means so simple, and can only be dealt with fully at a later stage. The data in the table indicate that cane sugar, urea, acetone, etc., are present as single molecules in solution, but hydrochloric acid, potassium nitrate, etc., behave as if there were nearly double the number of molecules to be anticipated from the formulæ. When van't Hoff put forward his theory of solutions he was quite unable to account for this behaviour, and contented himself with putting in the general gas equation a factor, *i*, to represent the abnormally high osmotic pressure, so that for salts and the so-called "strong" acids and bases in aqueous solution the equation became

$$PV = iRT.$$

The factor *i* can of course be obtained for aqueous solutions by dividing the experimental value of the molecular depression by the normal constant, 18·6, so that for potassium nitrate, for example, $i = 35{\cdot}8/18{\cdot}6 = 1{\cdot}92$.

Van't Hoff recalled the fact that ammonium chloride, in the form of vapour, exerts an abnormally high pressure, which is simply accounted for by its dissociation according to the equation $NH_4Cl = NH_3 + HCl$, but it did not appear that the results with salts, etc., could be explained in an analogous way. We shall see in detail later that the elucidation of the significance of the factor *i* was of the highest importance for the further development of the theory of solution. According to our present views, the substances which show abnormally high osmotic pressures are partially dissociated in solution, not into ordinary atoms, but into atoms or groups of atoms associated with electrical charges. The equation representing the partial splitting up of potassium nitrate, for example, may be written $KNO_3 = \overset{+}{K} + \overline{NO}_3$, which indicates that the solution contains potassium atoms associated with positive electricity, and an equal number of NO_3 groups, associated with negative electricity. These charged atoms, or groups of atoms, are termed *ions*.

Practical Illustrations. *Osmotic pressure*—The nature of semi-permeable membranes may readily be illustrated by Traube's experiment, described on page 109, and also by allowing drops of a fairly concentrated solution of potassium ferrocyanide to fall into a moderately dilute solution of copper sulphate in such a way that the drops, which are immediately surrounded by a film of copper ferrocyanide, remain suspended at the surface of the solution. It will be observed that the cells grow fairly rapidly owing to passage inwards of water from the copper sulphate solution, and, further, that in consequence of the increased concentration of the copper sulphate solution round the drop, the concentrated solution slowly flows down through the less concentrated solution. The stream of concentrated solution can readily be recognised by the difference of refractivity, especially if a bright light is placed behind the vessel

Selective Action of Semi-permeable Membrane.—This can be illustrated by Nernst's experiment, which is fully described and figured on page 117.

A simple experiment illustrating the same principle has been described by Kahlenberg.[1] At the bottom of a cylindrical jar is placed a layer of chloroform, above that a layer of water, and at the top a layer of ether and the jar is then corked. After some time it will be noticed that the chloroform layer has increased in depth, the water layer having moved higher up the tube. This phenomenon depends on the fact that ether is much more soluble in water than chloroform. The water therefore acts like a semi-permeable membrane, absorbing the ether and giving it up to the chloroform. At the same time the chloroform is dissolving in the water and passing through to the ethereal layer, but owing to its much smaller solubility, the current upwards is negligible in comparison with that downwards.

In the same paper, Kahlenberg describes a number of experiments with rubber membranes, which are in many respects instructive.

Separation of Solvent and Solute in Freezing-point Experiments—This point, which is of fundamental importance for the

[1] *J. Physical Chem.*, 1906., **10**, 141.

applicability of the freezing-point method of determining molecular weights, can be illustrated by partially freezing an aqueous solution of a highly coloured substance such as potassium permanganate (0·1 per cent. solution). When the solution is poured off, it will be found that the ice which has separated is practically colourless.

The determination of molecular weights by the boiling-point method (p. 126) and by the freezing-point method (p. 130) are fully described in the course of the chapter.

APPENDIX

Mathematical Deductions of Formulæ Connecting Osmotic Pressure with Other Properties of Solutions

In the course of the present chapter, several formulæ of fundamental importance have been made use of, and their meaning has been fully illustrated by numerical examples. For the sake of the more advanced student, simple deductions of these formulæ are given. It must be understood that the deductions are not mathematically strict, as certain of the assumptions on which they are based are only approximately true.

Lowering of Vapour Pressure—The fundamental equation (p. 122),

$$\frac{p_1 - p_2}{p_1} = \frac{M}{sRT} \cdot P \quad . \quad . \quad . \quad . \quad (1)$$

which gives the connection between the relative lowering of vapour pressure and the osmotic pressure, and the Raoult-van't Hoff formula (p. 122),

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is readily derived from equation (1) by means of the gas laws, can be deduced by a statical-thermodynamical method due to Arrhenius and also by a cyclical thermodynamical method due to van't Hoff. These deductions will now be given.

(1) *The Statical Method*—A long tube, R, containing a solution of n mols of a non-volatile solute in N mols of solvent,[1] is closed at its lower end by a semi-permeable membrane and placed upright in a vessel, C, which contains pure solvent (Fig. 22). The arrangement is covered by a bell-jar and all air is removed from the interior. When equilibrium between solvent and solution is established through the semi-permeable membrane it is evident that the osmotic pressure is measured by the hydrostatic pressure of the column of liquid (height, h) in the tube. Now the pressure of vapour at the level, a, of the surface of the solution must be the same

[1] In calculating the number of mols of solvent, its molecular weight, M, is taken as that in the form of vapour (p. 122).

inside and outside the tube. If this were not the case, evaporation or condensation of vapour would take place at the surface, *a*, and in either case the concentration of the solution would be altered and the equilibrium between solution and solvent disturbed, which is contrary to the origi al postulate that the system is in equilibrium. If p_1 is the vapour pressure of the solvent and p_2 that of the solution, the difference $p_1 - p_2$ is the difference of pressure at the surface of the solvent and at the level, *a*. This difference is due to the weight of a column of vapour of height, *h*, on unit area, therefore

$$p_1 - p_2 = hd \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where *d* is the density of the vapour.

We have now to express *d* an *h* in a different form. If v_1 is the volume of 1 mol of the vapour, and M the molecular weight of the vapour *in the gaseous form*, we have $d = M/v_1$ or $v_1 = M/d$. When this value of v_1 is substituted in the general gas equation $p_1 v_1 = RT$, we obtain

$$d = \frac{Mp_1}{RT}.$$

Further, as the osmotic pressure, P, is measured by the weight of the column, *h*, therefore $P = hs'$ where s' is the density of the solution. If very dilute solutions are used, no appreciable error will be committed by substituting *s*, the density of the solvent, for s', the density of the solution. Substituting these values of *d* and *h* in equation (*a*) we obtain

$$p_1 - p_2 = \frac{P}{s}\frac{Mp_1}{RT}$$

or

$$\frac{p_1 - p_2}{p_1} = \frac{M}{sRT} . P,$$

which is equation (1), p. 122.

From this equation, we obtain the formula,

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N}$$

as already described (p. 122).

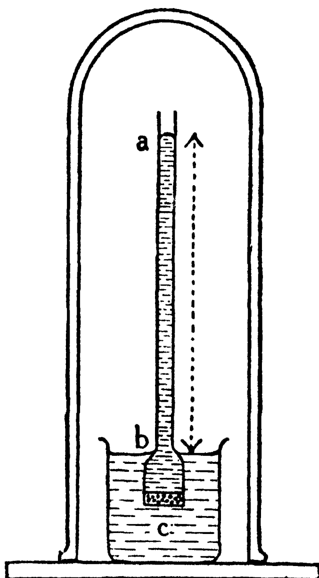


FIG. 22.

(2) *The Cyclical Method*—This thermodynamical proof of the above formula depends upon the performance of a cyclic process—in which the system is finally brought back to its initial condition—reversibly at constant temperature. The fundamental point to bear in mind in connection with such processes is that they must be conducted throughout under equilibrium conditions. It has already been pointed out (p. 120) that the thermodynamical proof of the connection between osmotic pressure and the lowering of vapour pressure depends on the work done in removing solvent reversibly from a solution. There are two principal methods by which removal (or addition) of solvent can be accomplished :—

(*a*) If the solution is brought into contact with its own saturated vapour at constant temperature, the slightest diminution of the external pressure will effect the removal of part of the solvent; on the other hand, the slightest increase of the external pressure will bring about condensation of vapour. If the change of volume of the solution is in each case very small compared with the total volume, the change in concentration can be neglected.

(*b*) A solution is placed in a cylinder closed at the bottom with a semi-permeable membrane, the cylinder is immersed in the pure solvent, and a movable piston rests on the upper surface. The solution and solvent will be in equilibrium through the semi-permeable membrane when the pressure on the piston is equal to the osmotic pressure. If the pressure is diminished ever so slightly by raising the piston, solvent will enter; if the pressure on the piston is slightly increased, solvent will pass out through the membrane. We have, therefore, a second method by which solvent can be separated from a solution in a reversible manner, equilibrium being maintained throughout. The cyclic process, in which both these methods are used, will now be described.

(1) From a solution containing n mols of solute to N mols of solvent, a quantity of solvent which originally contained 1 mol of solute is squeezed out reversibly by means of the piston and cylinder arrangement; the quantity thus removed is N/n mols. As the original quantity of solution is supposed to be very great, its concentration, and therefore its osmotic pressure, are not appreciably altered in the process. As the volume removed is that which contained 1 mol of solute, the work done on the system, which is the product of the change of volume and the pressure on the piston (the osmotic pressure), is equal to

$$-RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

(p. 34) if the gas laws apply.

(2) The quantity of solvent is now converted reversibly into vapour by expansion at the pressure, p_1, of the solvent; the work gained is approximately p_1v_1 for 1 mol of vapour (the volume of the liquid being regarded as negligible in comparison), or

$$\frac{N}{n}p_1v_1 \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

altogether.

(3) The vapour is now allowed further to expand till its pressure falls to p_2, the vapour pressure of the solution: in this process, an amount of work is done by the system represented approximately by

$$\frac{p_1 + p_2}{2}(v_2 - v_1)$$

per mol of vapour, where $(p_1 + p_2)/2$ is the mean pressure during the small expansion. The quantity of vapour actually used is N/n mols, hence the total work done by the system is

$$\frac{N}{n}\left(\frac{p_1 + p_2}{2}\right)(v_2 - v_1) \quad . \quad . \quad . \quad . \quad (iii)$$

(4) The vapour, at the pressure p_2, is now brought into contact with the solution with which it is in equilibrium and condensed reversibly, so that the system regains its initial state. The work done on the system in condensing the gas to liquid at the pressure p_2 is approximately

$$-\frac{N}{n}p_2v_2 \quad . \quad . \quad . \quad . \quad . \quad (iv)$$

As the entire cycle is carried through at constant temperature, there has on the whole been no transformation of heat into work or *vice versâ;* as the system is finally brought back to its initial condition, the work done on the system must on the whole be equal to the work done by the system; in other words (i) + (ii) + (iii) + (iv) must be zero.

Combining in the first place (ii), (iii), and (iv), we have

$$\frac{N}{n}p_1v_1 + \frac{N}{n}\left(\frac{p_1 + p_2}{2}\right)(v_2 - v_1) - \frac{N}{n}p_2v_2,$$

which reduces to

$$\frac{N}{n}\left(\frac{v_2 + v_1}{2}\right)(p_1 - p_2) = \frac{N}{n}v(p_1 - p_2)$$

where v is the mean volume of 1 mol of vapour.

Substituting for v its value from the general gas equation, $v = RT/p$, we have finally[1]

$$\frac{N}{n} . RT\frac{p_1 - p_2}{p_1}$$

as the work done by the system in the last three stages of the cycle. This must be equal to the work done on the system during the osmotic removal of solvent, hence

$$\frac{N}{n} . RT\frac{p_1 - p_2}{p_1} - RT = 0$$

or

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N}$$

as before.

The same result may be obtained still more simply by integration. The work done by the system in step (ii) is exactly balanced by that done on the system in (iv), as is evident from the factors themselves, if the gas laws hold. In (iii) both the pressure and the volume change during the expansion, hence work done by the system for 1 mol of vapour is equal to

$$\int_{v_1}^{v_2} p\,dv = \int_{v_1}^{v_2} RT\frac{dv}{v} = RT\log_e\frac{v_2}{v_1} = RT\log_e\frac{p_1}{p_2} \text{ (since } p_1v_1 = p_2v_2)$$

$$= -RT\log_e\frac{p_2}{p_1} = -RT\log_e\left(1 - \frac{p_1 - p_2}{p_1}\right) = RT\frac{p_1 - p_2}{p_1}$$

approximately,[2] or, for the total volume of vapour,

$$\frac{N}{n}RT\frac{p_1 - p_2}{p_1}.$$

The remainder of the proof is as above.

[1] When the solution is dilute, p in the denominator may be put equal to p_1 without sensible error.

[2] $RT\frac{p_1 - p_2}{p_1}$ is the first term of the expansion of the logarithmic function. The more accurate form of the van't Hoff-Raoult formula is $\log_e p_1/p_2 = \frac{n}{N}$, to which the usual form approximates in dilute solution.

Lowering of Freezing-point—The above formula has been deduced by an isothermal cyclic process, but the cyclic process by which the freezing-point formula is deduced cannot be carried through at constant temperature. We are therefore concerned with a new question, that of the relationship between heat and work. The law which applies in this case is the second law of thermodynamics, the deduction of which is to be found in any advanced book on Physics, and which states that the maximum work, dA, obtainable from a given quantity of heat, Q, in a reversible cycle is given by

$$dA = q\frac{dT}{T}$$

where the symbols have the usual significations (p. 158).

A solution containing n mols of solute in N mols (W grams) of solvent is contained in the cylinder with semi-permeable membrane and movable piston already described. The freezing-point of the solvent is taken as T and that of the solution as $T - dT$. The stages in the cyclic process are as follows:—

(1) At the temperature $T - dT$ an amount of solvent which originally contained 1 mol of solute is frozen out; the amount in question is N/n mols or MN/n grams. The separation can be carried out at constant temperature provided that the amount of solution is so great that its concentration is not thereby appreciably affected. The solidified solvent is then separated from the solution and the temperature of both raised to T.

(2) The solidified solvent is fused, in which process $H \, . \, \frac{MN}{n}$ calories are taken up, H being the heat of fusion per gram.

(3) The fused solvent is then brought into contact with the solution through the semi-permeable membrane under equilibrium conditions, that is, when the pressure on the piston is equal to the osmotic pressure of the solution (p. 138) and is allowed to mix reversibly with the solution. The work done by the system in this process is represented by the product of the osmotic pressure, P, and the volume, v, in which 1 mol of solute was dissolved and is, therefore, according to the gas laws, equal to RT.

(4) The system is finally cooled to the original temperature, $T - dT$ in order to complete the cycle.

We have now to consider the work done in the different stages of the cycle. The heat expended in warming solution and solvent in (1) is practically compensated[1] by the heat given out in (4). Further, an amount of heat HW/n is taken in at the higher temperature, T, and a somewhat less amount given out at $T - dT$; hence, by the second law of thermodynamics, the work done on the system is

$$H \, . \, \frac{W}{n} \, . \, \frac{dT}{T}.$$

The only work done by the system is that expended in the osmotic readmission of the solvent, hence

$$RT = H \, . \, \frac{W}{n} \, . \, \frac{dT}{T}$$

or

$$dT = \frac{RT^2}{H} \, . \, \frac{n}{W} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] The two amounts are not exactly equal, but the difference can be made negligible in comparison with the heat taken up in the second stage of the cycle.

If instead of H we use the *molecular* heat of fusion, λ, we have $\lambda = MH$, and, further, $N = W/M$. Substituting these values in equation (1), the latter reduces to

$$dT = \frac{RT^2}{\lambda} \cdot \frac{n}{N} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this it is evident that the lowering of the freezing-point, like the relative lowering of vapour pressure, is proportional to the ratio of the number of mols of solute to the number of mols of solvent.

From the above formula, or more readily from equation (1), above, an expression for K, the depression produced when 1 mol of solute is dis solved in 100 grams of solvent, can readily be obtained. R is approximately = 2 when expressed in calories, $n = 1$ and $W = 100$. Hence we obtain, for this particular value of dT,

$$dT = K = \frac{2T^2}{H} \cdot \frac{1}{100} = \frac{0{\cdot}02T^2}{H} \quad . \quad . \quad . \quad (3)$$

which is the formula given on p. 125.

Elevation of Boiling-point—By means of a cyclic process exactly corresponding with that already used in establishing the freezing-point formula, the formula connecting the elevation of the boiling-point with the latent heat of vaporization of the solvent is obtained in the form

$$dT = \frac{0{\cdot}02T^2}{H}$$

where H is the heat of vaporization of 1 gram of solvent at the temperature of the experiment, and T is the boiling-point of the solvent on the absolute scale.

Summary of Formulæ—(*a*) *Osmotic Pressure and Relative Lowering of Vapour Pressure.*—Formula (1), p. 122, connecting osmotic pressure and relative lowering of vapour pressure, may be written

$$P = \frac{sRT}{M} \cdot \frac{p_1 - p_2}{p_1}$$

where P is the osmotic pressure, s is the density of the solvent at the absolute temperature, T, M is the molecular weight of the solvent in the form of vapour, and p_1 and p_2 are the vapour pressures of solvent and solution respectively.

In order to obtain P in atmospheres, the volume of 1 mol of the solvent M/s has to be expressed in litres and becomes $\frac{M}{1000s}$. The value of R, in litre atmospheres is 0·0821. Substituting in the above formula we obtain

$$P = \frac{0{\cdot}0821T \ 1000s}{M} \cdot \frac{p_1 - p_2}{p_1}$$

where P is the osmotic pressure in atmospheres and the other symbols have the signification stated above.

(*b*) *Osmotic Pressure and Lowering of Freezing-point*—Formula (1), p. 140, connecting osmotic pressure and lowering of freezing-point may be written

$$dT = \frac{RT^2}{H} \cdot \frac{n}{MN}.$$

Substituting for n its value from the equation

$$P = \frac{nRTs}{MN}$$

we obtain

$$P = Hs\frac{dT}{T}.$$

In order to o' tain P in atmospheres, the volume of a mol of the solvent has to be expressed in litres, which introduces the factor 1000, and the factor 24·22 has to be brought in to convert calories to litre atmospheres (1 litre atmosphere = 24·22 calories). We thus obtain

$$P = \frac{1000Hs}{24{\cdot}22} \cdot \frac{dT}{T}$$

where H is the latent heat of fusion of the solvent in calories per gram, T is the freezing-point of the solvent on the absolute scale and dT is the freezing-point depression.

Osmotic Pressure and Elevation of Boiling-point—The formula, which corresponds exactly with that for the freezing-point depression, is

$$P = \frac{1000Hs}{24{\cdot}22} \cdot \frac{dT}{T}$$

where H is the latent heat of vaporization for 1 gram of solvent at its boiling-point, T is the boiling-point of the solvent on the absolute scale, and dT is the boiling-point elevation.

CHAPTER VI

THERMOCHEMISTRY

General—It is a matter of everyday experience that chemical changes are usually associated with the development or absorption of heat. When substances enter into chemical combination very readily, much heat is usually given out (for example, the combination of hydrogen and chlorine to form hydrogen chloride), but when combination is less vigorous, the heat given out is usually much less, and, in fact, heat may be absorbed in a chemical change. These facts, which were noticed very early in the history of chemistry, led to the suggestion that the amount of heat given out in a chemical change might be regarded as a measure of the chemical affinity of the reacting substances. Although, as will be shown later, this is not strictly true, there is, in many cases, a parallelism between chemical affinity and heat liberation. In thermochemistry, we are concerned with the heat equivalent of chemical changes.

Heat is a form of energy, and therefore the laws regarding the transformations of energy are of importance for thermochemistry. It is shown in text-books of physics that there are different forms of energy, such as potential energy, kinetic energy, electrical energy, radiant energy, and heat, and that these different forms of energy are mutually convertible. Further, when one form of energy is converted completely into another, there is always a definite relation between the amount which has disappeared and that which results. The best-known example of this is the relation between kinetic energy and heat, which has been very carefully investigated by Joule, Rowland, and others. Kinetic energy may be measured in gram-centimetres or in ergs, and heat energy in calories (see p. xix). The investigators just referred to found that

1 calorie = 42,650 gram-centimetres = 41,830,000 ergs, an equation representing the mechanical equivalent of heat. From the above considerations it follows that when a certain amount of one form of energy disappears an equivalent amount of another form of energy makes its appearance. These results are summarized in a law termed the *Law of the Conservation of Energy*, which may be expressed as follows: *The energy of an isolated system is constant*, i.e., *it cannot be altered in amount by interactions between the parts of the system.* The proof of this law lies in the *experimental* impossibility of perpetual motion—it has been found impossible to construct a machine which will perform work without the expenditure of energy of some kind.

In dealing with chemical changes, it has been found convenient to employ the term chemical energy, and when two substances combine with liberation of heat, we say that chemical energy has been transformed to heat. To make this clear, we will consider a concrete case, the burning of carbon in oxygen with formation of carbon dioxide, a reaction which, as is well known, is attended with the liberation of a considerable amount of heat. The reaction can be carried out under such conditions that the heat given out when a definite weight of carbon combines with oxygen can be measured, and it has been found that when 12 grams of carbon and 32 grams of oxygen unite, 94,300 calories are liberated. This result may conveniently be represented by the equation



$$C + O_2 = CO_2 + 94{,}300 \text{ cal.}$$

in which the symbols represent the atomic weights of the reacting elements in grams. The above equation is an illustration of the conversion of chemical energy into heat—12 grams of free carbon and 32 grams of free oxygen possess 94,300 cal. more energy than the 44 grams of carbon dioxide formed by their union. From these and similar considerations it follows that the free elements must have much intrinsic energy, but the absolute amount of this energy in any particular case is quite unknown. Fortunately, this is a matter of secondary importance, as chemical changes do not depend on the *absolute amounts* of energy, but only on the *differences* of energy of the reacting systems.

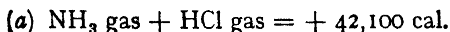
So far, we have implicitly assumed that the increase or decrease of internal energy when a system A changes to a system B is measured by the heat absorbed or given out during the reactions; but this is not necessarily the case. In particular, external work may be done during the change, by which part of the energy is used up, or heat may be produced at the expense of external work (*cf.* p. 34). If the total diminution of internal energy in the change A→B is represented by U, the heat given out by $-q$, and the external work done by the reacting substances during the transformation by A, we have, by the principle of the conservation of energy,

$$U = A - q.$$

When no external work is done the total diminution of energy, U, is numerically equal to Q, the heat evolved in the reaction. The factor A is only of importance when gases are involved in the chemical change.

Hess's Law—It is an experimental fact that when the same chemical change takes place between definite amounts of two substances under the same conditions the same amount of heat is always given out provided that the final product or products are the same in each case. Thus when 12 grams of carbon combine with 32 grams of oxygen with formation of carbon dioxide, 94,300 cal. are always liberated, quite independently of the rate of combustion or of the nature of the intermediate products. This law was first established experimentally by Hess in 1840, and may be illustrated by the conversion, by two different methods, of a system consisting of 1 mol of ammonia and of hydrochloric acid respectively and a large amount of water, each taken separately, into a system consisting of 1 mol of ammonium chloride in a large excess of water. By the first method we measure (*a*) the heat change when 1 mol of gaseous ammonia and 1 mol of gaseous HCl combine, (*b*) the heat change when the solid ammonium chloride is dissolved in a large excess of water; by the second method we measure the heat changes when (*c*) 1 mol of ammonia, (*d*) 1 mol of hydrochloric acid are dissolved separately in excess of water, and (*e*) when the two solutions are mixed. The results obtained were as follows:—

First Way


(*a*) NH_3 gas + HCl gas = + 42,100 cal.

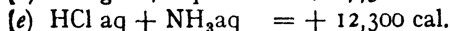

(*b*) NH_4Cl + aq = − 3,900 cal.

38,200 cal.

Second Way


(*c*) NH_3 gas + aq = + 8,400 cal.


(*d*) HCl gas + aq = + 17,300 cal.


(*e*) HCl aq + NH_3aq = + 12,300 cal.

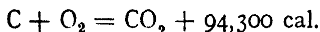
38,000 cal.

As will be seen, $a + b = c + d + e$ within the limits of experimental error.

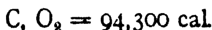
It can easily be shown that Hess's law follows at once from the principle of conservation of energy.

This law is of the greatest importance for the indirect determination of the heat changes involved in certain reactions which cannot be carried out directly. For example, we cannot determine directly the heat given out when carbon combines with oxygen to form carbon monoxide. The heat given out when 12 grams of carbon burn to carbon dioxide is 94,300 cal., which is, by Hess's law, equal to that produced when the same amount of carbon is burned to monoxide and the latter then converted to dioxide. The latter change gives out 68,100 cal., and the reaction C + O = CO must therefore be associated with the liberation of 94,300 − 68,100 = 26,200 cal.

Representation of Thermochemical Measurements. Heat of Formation. Heat of Solution—As has already been pointed out, the results of thermochemical measurements may be conveniently represented by making the ordinary chemical equation into an energy equation, for example

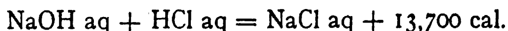

$$C + O_2 = CO_2 + 94{,}300 \text{ cal.}$$

Sometimes, if the final condition of the system is assumed to be known, the shorter form


$$C, O_2 = 94{,}300 \text{ cal.}$$

may be used.

When, as is frequently the case, the reacting substances are used in aqueous solution, this is indicated by adding aq to the formula in question. Thus the neutralization of dilute hydrochloric acid by sodium hydroxide is represented as follows :—



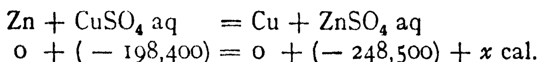
$$NaOH\ aq + HCl\ aq = NaCl\ aq + 13{,}700\ cal.$$

The heat of formation of a compound is the heat given out when a mol of the compound is formed from its component elements. Thus the heat of formation of carbon dioxide (at constant volume) is 94,300 cal. The above energy equations, *e.g.*, that representing the formation of carbon dioxide, are, however, not complete, inasmuch as we do not know the intrinsic energy associated with free carbon and oxygen respectively, nor do we know the differences of energy between the various elements, as they are not mutually convertible by any known means. We may therefore choose any arbitrary values for the intrinsic energies of the elements, and it has been found most convenient to put them all equal to zero. On this basis the intrinsic energy of carbon dioxide, being 94,300 cal. less than the sum of the intrinsic energies of the component elements, is − 94,300 cal., and, in general, the intrinsic energy of a compound is numerically equal to its heat of formation, but with the sign reversed.

When the heats of formation of all the substances taking part in a reaction are known, the heat set free in the reaction can be calculated. One method of doing so is to apply the law that the heat of reaction is equal to the sum of the heats of formation of the substances formed minus the sum of the heats of formation of the substances used up. This law follows at once if we imagine the reacting substances first decomposed into their elements and these elements then combined to form the final products. In the first stage there would be *absorbed* an amount of heat equal to the sum of the heats of formation of the reacting substances, and in the second stage an amount of heat would be *given out* equal to the sum of the heats of formation of the products.

An alternative method, the basis of which will be evident on a little consideration, is to write an energy equation in which the formulæ of the various compounds are replaced by their

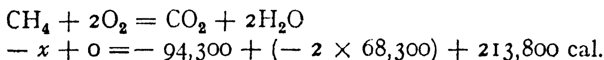
intrinsic energies (the respective heats of formation with the signs reversed). As an example of the method, we may calculate the heat of reaction, x, when copper is displaced from copper sulphate in dilute solution by metallic zinc. The heat of formation of copper sulphate (from its elements) in dilute solution is 198,400 cal. and of zinc sulphate under the same conditions 248,500 cal. The energy equation for the chemical change is therefore



$$\begin{aligned} Zn + CuSO_4\,aq &= Cu + ZnSO_4\,aq \\ 0 + (-198{,}400) &= 0 + (-248{,}500) + x \text{ cal.} \end{aligned}$$

whence x, the total heat liberated in the reaction, is $248{,}500 - 198{,}400 = 50{,}100$ cal.

In the same way an unknown heat of formation can be calculated when all the other heats of formation and the heat of reaction are known—a method which, as shown in the last section, is particularly useful for obtaining the heats of formation of substances such as carbon monoxide and methane, which cannot be determined directly. As an example, the heat of formation of methane will be calculated. The heat given out when 1 mol of this compound is burned completely in oxygen is 213,800 cal., and the heat of formation of the products, carbon dioxide and water, are 94,300 and 68,300 cal. respectively. Representing the heat of formation of methane by x, its intrinsic energy therefore by $-x$, we have the equation



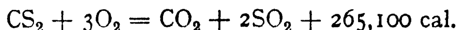
$$\begin{aligned} CH_4 + 2O_2 &= CO_2 + 2H_2O \\ -x + 0 &= -94{,}300 + (-2 \times 68{,}300) + 213{,}800 \text{ cal.} \end{aligned}$$

Whence $x = 17{,}100$ cal.

A compound such as methane, which is formed with liberation of heat, is termed an *exothermic* compound, whilst one which is formed with absorption of heat is termed an *endothermic* compound.

The majority of stable compounds are exothermic. Among the best-known endothermic compounds are carbon disulphide, hydriodic acid, acetylene, cyanogen, and ozone. It is not always easy to determine directly whether a compound is exothermic or endothermic, but this may be done indirectly

by carrying out a chemical change with the compound itself and with the components separately and comparing the heat changes in the two cases. The method may be illustrated by reference to carbon disulphide. When burnt completely in oxygen, the gaseous compound gives out 265,100 cal. according to the equation



$$CS_2 + 3O_2 = CO_2 + 2SO_2 + 265{,}100 \text{ cal.}$$

Hence, representing the intrinsic energy of the compound by $-x$, we have, for the energy equation,

$$-x + 0 = +(-94{,}300) + (-2 \times 71{,}000) + 265{,}100,$$

and $-x = +28{,}800$ cal. The intrinsic energy of carbon disulphide is therefore 28,800 cal.; that is, the compound has 28,800 cal. more energy than the elements from which it is formed.

The *heat of solution* is the quantity of heat given out or absorbed by the solution of a mol of the substance in so much of the solvent that no further heat change is observed when more of the solvent is added. The heat of solution as thus defined is usually different from the heat change observed when a mol of substance is dissolved in sufficient solvent to form a saturated solution, and the two quantities may even be of opposite sign. Thus the heat of solution of cupric chloride dihydrate, $CuCl_2$, $2H_2O$, is positive in dilute and negative in very concentrated solution. It is the heat of solution in nearly saturated solution which is of importance in predicting the effect of temperature on the solubility in accordance with Le Chatelier's theorem (p. 176).

It has already been mentioned (p. 145) that the heat given out in a chemical change differs according to whether changes of volume occur with the consequent performance of internal work by or on the system. When only solids and liquids are concerned, no appreciable changes of volume occur and the internal work is negligible. When gases are concerned, however, the heat change at constant volume, when no internal work is done, may differ considerably from that at constant pressure.

As already pointed out (p. 34) when a mol of gas is generated at the absolute temperature, T, work is done by the system and

RT calories is absorbed; when, on the other hand, a mol of gas disappears RT calories is given out. A little consideration will show that if Q_v is the heat of reaction in calories at constant volume (when no external work is done) and Q_p the heat of reaction at constant pressure (when external work may be done) the relationship between Q_v and Q_p is given by the formula

$$Q_p = Q_v + (n_1 - n_2)RT$$

where n_1 and n_2 represent the number of mols of gas in the initial and final stages of the reaction respectively.

For example, the reaction $2H_2 + O_2 \rightarrow 2H_2O$ (liquid) gives $2 \times 68{,}400$ calories at constant pressure and therefore the heat of reaction at constant volume at 17° is given by the equation

$$68{,}400 = Q_v + 1\tfrac{1}{2} \times 580, \text{ and } Q_v = 67{,}530 \text{ cal.}$$

for 18 grams of water.

The heats of formation at constant volume of some important compounds are given in the accompanying table. The statements in brackets refer either to the state of the reacting substances or of the product:—

Substance.	Heat of Formation (Calories).
H_2O (liquid)	+ 67,530
CO_2 (diamond)	+ 94,300
CO (diamond)	+ 26,600
SO_2 (rhombic sulphur)	+ 71,080
HF (gaseous fluorine)	+ 38,600
HCl (gaseous chlorine)	+ 22,000
HBr (liquid bromine)	+ 8,400
HI (solid iodine)	− 6,100
NH_3	+ 12,000
NO	− 21,600
NO_2	− 7,700
KCl	+ 105,600
KBr	+ 95,300

Heat of Combustion—Whilst a great many inorganic reactions are suitable for thermochemical measurements, this is not in general the case for organic reactions; in fact, the only reaction which is largely used for the purpose is combustion in

oxygen to carbon dioxide and water. The heat given out when a mol of a substance is completely burned in excess of oxygen is termed the *heat of combustion*, and from this, by application of Hess's law, the heats of formation can be calculated, as has been done for methane and carbon disulphide, in the preceding section. Further, the heat given out in a chemical change can readily be calculated by Hess's law when the heats of combustion of the reacting substances are known—it will clearly be equal to the sum of the heats of combustion of the substances which disappear less the sum of the heats of combustion of the substances formed. As an example, the heat of formation of ethyl acetate from ethyl alcohol and acetic acid may be calculated. The heat of combustion of ethyl alcohol is 34,000 cal., of acetic acid 21,000 cal., and of ethyl acetate 55,400 cal., whence the heat of formation of ethyl acetate is $34{,}000 + 21{,}000 - 55{,}400 = -400$ cal.

Thermochemical Methods—Two principal methods are employed in measuring the heat changes associated with chemical reactions. If the reaction takes place in solution, the water calorimeter, so largely used for purely physical measurements, may be employed. For the determination of heats of combustion, on the other hand, in which solids or liquids are burned completely in oxygen, special apparatus has been designed by Thomsen, Berthelot, Favre, and Silbermann, and others.

(*a*) *Reactions in Solution*—The change (chemical reaction, dilution or dissolution), the thermal effect of which is to be measured, is brought about in a test-tube deeply immersed in a large quantity of water, and the rise of temperature of the water is measured with a sensitive thermometer. When the weight of the water and the heat capacity of the calorimeter are known, the heat given out in the reaction can readily be calculated. Allowance must, of course, be made for the heat capacity of the solution in the test-tube.

A simple modification of Berthelot's calorimeter, used by Nernst, is shown in Fig. 23. It consists of two glass beakers, the inner one being supported on corks, as shown, and nearly filled with water. Through the wooden cover, X, of the outer beaker pass a thin-walled test-tube, A, in which the reaction takes place, an accurate thermometer, B, and a stirrer, C, of

brass, or, better, of platinum. The water in the calorimeter is stirred during the reaction, which must be rapid, and the heat of reaction can then be calculated in the usual way when the weight of water in the calorimeter and the rise of temperature are known. Experiments on neutralization and on heat of solution are conveniently made in the inner beaker, the solution itself serving as calorimetric liquid. For dilute aqueous solutions, it is sufficiently accurate to assume that the heat capacity of the solution is the same as that of water.

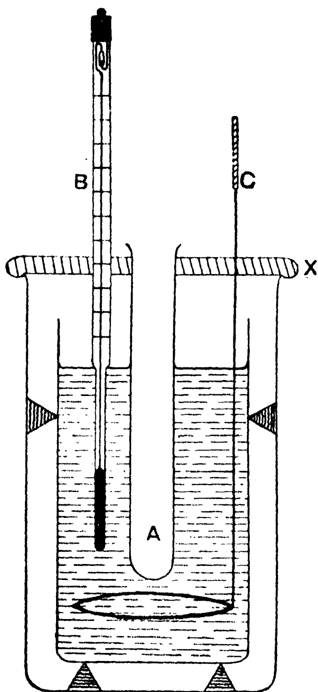


Fig. 23.

The chief source of error in the measurements is the loss of heat by radiation, which is minimized (*a*) by choosing for investigation reactions which are complete in a comparatively short time; (*b*) by making the heat capacity of the calorimeter system large. It is of advantage so to arrange matters that the temperature of the calorimeter liquid is 1-2° below the atmospheric temperature before the reaction, and 1-2° above it after the reaction.

(*b*) *Combustion in Oxygen*—This may conveniently be carried out in Berthelot's calorimetric bomb, a vessel of steel, lined with platinum and provided with an air-tight lid. The substance for combustion is placed in the bomb, which is filled with oxygen at 20-25 atmospheres' pressure. The whole apparatus is then sunk in the water of the calorimeter, and the combustion initiated by heating electrically a small piece of iron wire placed in contact with the solid.

Results of Thermochemical Measurements.—Some of the more important results of thermochemical measurements have already

been incidentally referred to in the preceding paragraphs. In stating the results of thermochemical measurements, the condition of the substances taking part in the reaction must always be clearly stated. This applies not only to the physical state, in connection with which allowance must be made for heat of vaporization, heat of fusion, etc., but also to the different allotropic modifications of the solid. Thus monoclinic sulphur has 2300 cal. more internal energy than rhombic sulphur, and yellow phosphorus 27,300 cal. more than the red modification.

The correction for change of state is often very great. For the transformation of water to steam at 100°, it amounts to about $537 \times 18 = 9566$ calories per mol. If, instead of the heat of formation of liquid water, which is 68,300 cal., the heat of formation of water vapour is required, it is $68,300 - 9570 = 58,730$ cal. in round numbers.

As regards the thermochemistry of salt solutions, one or two experimental results may be mentioned which will find an interpretation later. When dilute solutions of two salts, such as potassium nitrate and sodium chloride, are mixed, heat is neither given out nor absorbed. This important result is termed the *Law of thermoneutrality* of salt solutions (p. 284). Further, when a mol of any strong monobasic acid is neutralized by a strong base, the same amount of heat, 13,700 cal., is always liberated (p. 289).

The heat of formation of salts in dilute aqueous solution is obtained by the addition of two factors, one pertaining to the positive, the other to the negative part of the molecule; in other words, the heat of formation of salts in dilute solution is a distinctly additive property. The same is true to some extent for the heat of combustion of organic compounds. For example, the difference in the heat of combustion of methane and ethane is 158,500 cal., and in general, for every increase of CH_2, the heat of combustion increases by about 158,000 cal. From these and similar results, we can deduce the general rule that equal differences in composition correspond to approximately equal differences in the heat of combustion. We may go further, and obtain definite values for the heat of combustion of a carbon atom and a hydrogen atom as has already been done for atomic volumes; the molecular heat of combustion

is then the sum of the heats of combustion of the individual atoms. Experience shows that when allowance is made for double and triple bindings, the observed and calculated values for the heats of combustion of hydrocarbons agree fairly well.

Measurements of Specific Heats—A method of determining the specific heat of a gas at constant pressure has already been described (p. 51), and reference has been made to Joly's method of measuring specific heats of gases at constant volume. The principle of the method is that the gas, confined in a metal vessel, is raised through a certain range of temperature by steam passed round the outside of the vessel, the heat supplied being deduced from the weight of moisture condensed on the vessel.

For determinations at high temperatures the explosion method is used. The gas, the specific heat of which is to be obtained, is confined in a closed bomb together with a combustible gas and oxygen; the mixture is exploded and the maximum pressure in the bomb measured. From this the maximum temperature attained can be calculated and hence the heat capacity of the gaseous mixture, since the heat of reaction is known. One of the main difficulties is to determine the maximum pressure accurately, and sensitive manometers for this purpose have been devised.[1]

In recent years much attention has been devoted to the measurement of the specific heat of solids, especially at low temperatures. At temperatures from 0° C. upwards the ordinary method of mixtures gives satisfactory results, but for low temperature measurements special forms of apparatus have been devised by Nernst and his co-workers.

One form is illustrated in Fig. 24. It is based on the method of mixtures, a well-insulated copper block, KK, in a Dewar vessel, D, serving as the calorimeter. Changes of temperature are measured by thermo-elements, I, the lower junctions of which are inserted in K, the others in the copper cover, C. The whole apparatus is covered with thin copper sheeting and immersed in a constant temperature bath. The substance to be examined is introduced through the tube, RR, and the rise of temperature

[1] Pier, *Zeitsch. Elektrochem.*, 1909, **15**, 537; 1910, **16**, 897.

measured. This method gives the mean specific heat between two temperatures fairly wide apart.

The *vacuum calorimeter* is based on a different principle and enables specific heats to be determined within narrow intervals of temperature. The substance itself serves as the calorimeter; a measured quantity of electrical energy is supplied and the rise of temperature measured. The current is conveyed to the substance by a copper or platinum wire and the rise of temperature is determined from the change in resistance of the conducting wire. The apparatus is placed in an air-tight container which is immersed in a Dewar vessel containing the cooling liquid.

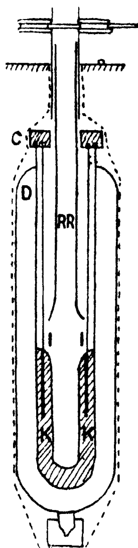


FIG. 24.

Reference has already been made to Dulong and Petit's law, according to which the atomic heat of solid elements is about 6·0. Boltzmann has shown that in the case of a monatomic crystalline solid at moderate temperatures the atomic heat, calculated according to the principles of the classical kinetic theory should be $3R = 5{\cdot}955$ calories; thus affording a theoretical basis for Dulong and Petit's law, discovered many years before. Certain exceptions to this law, however, have long been known (p. 10), and recent investigations have shown that at low temperatures the atomic heat falls much below the value 3R and would appear to become zero when the absolute zero is reached. This may be illustrated by means of the results obtained for carbon (diamond) and copper. The measurements were made at constant pressure and corrected to constant volume. The data for carbon extend over a wider range of temperature than those previously quoted.

Silver.

T abs. .	35°	43°	51°	77°	100°	273°	535°	589°
Mc_v .	1·59	2·22	2·81	4·07	4·72	5·77	5·90	5·92

Diamond.

T abs. .	30°	88°	205°	262°	331°	358°	413°	1169°
Mc_v .	0·000	0·006	0·62	1·16	1·82	2·07	2·53	5·19

It is a remarkable fact that the specific heat of the diamond is zero at temperatures considerably above the absolute zero.

Einstein (1907) applied the theory of quanta to the question of the specific heat of solids and showed that a rapid diminution of the atomic heat at low temperatures was to be anticipated. While Einstein's conclusions were confirmed in a qualitative way by the experiments of Nernst and his colleagues, there was no quantitative agreement, the specific heat falling off with lowering of temperature less rapidly than the Einstein formula requires. Nernst and Debye have suggested more complicated formulæ which show better agreement between theory and experiment than the original Einstein formula, but the problem has not been finally solved.

Relation of Chemical Affinity to Heat of Reaction—Very early in the study of chemistry, it becomes evident that chemical actions may be divided into two classes: (1) those which under the conditions of the experiment are spontaneous or proceed of themselves, once they are started, *e.g.*, the combination of carbon and oxygen; (2) those which only proceed when forced by some external agency, *e.g.*, the splitting up of mercuric oxide into mercury and oxygen. In this section we are concerned only with spontaneous changes.

The direction in which a chemical change takes place in a system depends on the energy relations of the system. We are accustomed to say that the direction of the change is determined by the *chemical affinity* of the reacting substances, and it is a matter of the utmost importance to obtain a numerical expression for the *chemical affinity* or *driving force* in a chemical system, the driving force being defined in such a way that the chemical change proceeds in the direction in which it acts, and comes to a standstill when the driving force is zero.

Most reactions in which there is a considerable transformation of chemical energy, and therefore a considerable development of other forms of energy, such as heat or electrical energy, proceed very rapidly (for example, the combination of hydrogen and chlorine), whilst reactions in which less chemical energy is transformed are usually much less vigorous (for example, the combination of hydrogen and iodine). It seems, therefore, at first sight plausible to measure the chemical affinity in a system

by the amount of heat liberated in the reaction (Thomsen, Berthelot). As, however, chemical affinity has been defined as acting in the direction in which spontaneous chemical change takes place, it would follow that only reactions in which heat is given out can take place spontaneously. This deduction is contrary to experience. Water can spontaneously pass into vapour, although in the process heat is *absorbed*, and many salts, such as ammonium chloride, dissolve in water with absorption of heat. It is clear, therefore, that chemical affinity, as above defined, cannot be measured by the total heat liberated in the reaction.

The importance for technical purposes of such a reaction as the burning of coal in oxygen is not so much the total heat obtainable by the change as the amount of work which the change may be made to perform. In a similar way, *it has been found convenient to measure the chemical affinity of a system by the maximum amount of external work which, under suitable conditions, the reaction may be made to perform.* This is a special case of a very comprehensive natural law, which may be expressed as follows: All spontaneous reactions (in the widest sense, including neutralization of electrical charges, falling of liquids to a lower level, etc.) can be made to perform work, and all reactions which can be made to perform work are spontaneous, *i.e.*, can proceed of themselves without the application of external forces. The available energy of a chemical reaction, that is, that part of the total energy which at constant temperature and under suitable conditions can be made to perform an equivalent of work, has been termed "free energy" by Helmholtz. The chemical affinity or driving force of a reaction is not proportional to the *total* change of energy, but to the change in the *available* or *free* energy.

The total energy, U, of a chemical change can be obtained in the form of heat by carrying out the reaction under such conditions that no external work is done (p. 145). We have now to consider what is the connection between the total decrease of energy, U, and the decrease of available or free energy, which may be termed A. This question is closely connected with the conditions under which heat can be continuously transformed into work. We have to find an expression

for the *maximum* work performed in a cycle in which the heat is taken in at the temperature, T, and given out at the slightly lower temperature, T — dT. The principle to be used for this purpose is that employed in the theory of the steam engine, but it has universal applicability. According to this, the maximum work, dA, obtainable from a given quantity of heat, Q, is given by

$$dA = Q\frac{dT}{T} \quad . \quad . \quad . \quad . \quad (1)$$

Equation (1) is the mathematical expression of the second law of thermodynamics.

The first law of thermodynamics may be expressed in the form (p. 145)

$$U = A - Q \quad . \quad . \quad . \quad . \quad (2)$$

in which A represents the external work done when the total diminution of energy is U and the heat given out is —Q. Now dA, in equation (1), is the difference of the maximum amounts of work obtainable in *isothermal* processes at the temperatures T and T — dT; thus A has the same significance here as in equation (2). We may therefore obtain an expression in which q does not occur by substituting for Q in equation (1) its value A — U, from equation (2). We thus obtain

$$A - U = T\frac{dA}{dT} \quad . \quad . \quad . \quad . \quad (3)$$

in which U represents the total change of energy in the reaction, A represents the free energy or chemical affinity, and dA/dT the rate of change of the free energy with temperature. Equation (3) is the fundamental equation for isothermal chemical changes, that is, for chemical changes which take place at constant temperature. The equation shows that the change in the free energy differs from the change in the total energy by an amount $Q = -T(dA/dT)$, and that the two quantities can only be identical when the right-hand side of the equation is zero. $Q = -T(dA/dT)$ is sometimes termed the *latent heat of the reaction*.

As the above equation has been derived from the second

law of thermodynamics, it follows that the free energy can be determined only for reactions which can be made completely reversible. By complete reversibility we mean that if a system in changing from the state A to B, performs an amount of work, X, it can be restored to the condition, A, by the expenditure of the same amount of work. Reactions such as the dissociation of calcium carbonate in a closed space by heat are reversible (p. 184), but a reaction in which gases escape from the system, as when zinc is dissolved in acid, is, of course, not reversible. Many reactions which are not reversible under ordinary conditions can be carried out reversibly in galvanic elements (for example, the displacement of copper from solution by zinc in the Daniell element), and therefore measurements of electromotive force are largely used for determinations of the free energy in a system. As will be shown later (p. 353), when a chemical reaction takes place reversibly in a galvanic cell, the electromotive force of the cell is proportional to the free energy of the reaction.

It is beyond the scope of this book to discuss fully the many deductions which may be made from equation (3), and only one important consequence will be mentioned. At the absolute zero ($T = 0$) the right-hand side of the equation becomes zero, and therefore the total change of energy, U (which is equal to the heat of reaction, Q, when no external work is done), is equal to the change in the free energy, A. In other words, at the absolute zero, all reactions would proceed in the direction in which heat is given out, and the heat evolved would *then* be a measure of the chemical affinity. As the absolute zero is at present unattainable, this statement by itself is of no practical importance, but the form of equation (3) indicates that at temperatures not very far from the absolute zero, U and A may often not be greatly different. As ordinary temperatures are relatively not very far from the absolute zero, we can now understand, from the approximation in the values of U and A, why so many chemical reactions proceed of themselves in the direction in which heat is given out (*cf* p. 143).

Although the dissolving of some salts in water is attended with absorption of heat, it can be shown that the free energy has diminished, and the same is true of the vaporization of water,

in these extreme cases, not only are A and U of very different numerical value, but they even have opposite signs.

Practical Illustrations—As already mentioned, the heat evolved in certain chemical reactions can conveniently be measured by causing the reaction to proceed in the glass tube, A, Fig. 24, and obtaining the heat of the reaction from the rise in temperature of the water. This form of apparatus is, however, more useful for measuring heats of dilution and of solution. If, for example, we wish to determine the heat of solution of potassium chloride, a known weight of water is placed in the inner beaker, a known weight of salt in the tube, A, and when the salt may be expected to be at the same temperature as the water, the glass tube is broken with a glass rod, the salt dissolved in the water by stirring, and the change of temperature read off on the thermometer.

For reactions in dilute solution, the tube A may be dispensed with, and the outer beaker supported on corks in a third beaker so as to minimize the loss of heat by radiation. In this apparatus the heat of neutralization of a dilute acid (half normal hydrochloric acid) by an equal volume of dilute alkali (sodium hydroxide) may be determined. $\frac{1}{4}$ litre of the hydrochloric acid is placed in the inner beaker, at a temperature 2° to 3° below that of the atmosphere, $\frac{1}{4}$ litre of N/2 sodium hydroxide, of known temperature, is rapidly poured into the acid with constant stirring. The highest temperature attained is noted. If the solutions are at the same temperature before mixing, the rise of temperature will be about 3·4°, corresponding with the fact that the heat of neutralization of 1 mol of sodium hydroxide by hydrochloric acid is 13,700 cal. (p. 153). Measurements of heat of neutralization, heat of dilution, etc., may be made still more conveniently with metal calorimeters, as used in physical laboratories; the vessels should be well polished so as to minimize the loss of heat by radiation.

Measurements should also be made with some form of combustion calorimeter, if available.

CHAPTER VII

EQUILIBRIUM IN HOMOGENEOUS SYSTEMS. LAW OF MASS ACTION

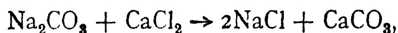
General—In the last chapter we have been mainly concerned with the heat equivalents of chemical charges. We have now to deal with chemical transformations, with reference more particularly to the dependence of the rate and extent of chemical reactions on the conditions.

When a chemical reaction can take place between two substances, it is usual to say that they have a certain "chemical affinity" for each other. From very early times the question as to the nature of this affinity has been discussed, but up to the present with very little success. Newton was of opinion that the small particles of different kinds attract each other much as the heavenly bodies do (gravitational attraction), and that the attraction falls off very rapidly with the distance. According to this view, if we have three substances, A, B, and C, and the attraction between A and B is greater than that between A and C, then B will completely displace C from its combination with A; in other words, the reaction $AC + B \rightarrow AB + C$ will be complete in the direction indicated by the arrow. These views found their expression in the so-called affinity tables drawn up by Stahl, Bergmann, and others, in which the elements were arranged in the order in which they could displace each other from combination. Somewhat later, Berzelius developed his electrochemical theory, according to which the attractions concerned in chemical changes are electrical in character, but this theory proved in many respects unsatisfactory. The importance of the *conditions*, more particularly as regards the relative amounts of the reacting substances and the temperature, on

the direction and amount of chemical change, only came to be recognized very gradually.

In recent years, the question as to *why* certain chemical changes take place has been relegated to the background and attention has been directed to *how* they take place. As mentioned in the last chapter, it has been found possible in many cases to obtain numerical values for the chemical affinity, without troubling about its exact nature. When for any reaction the chemical affinities of the reacting substances are known, as well as the dependence of the reaction on the conditions, the reaction is completely described.

Law of Mass Action—The importance of the relative amounts of the reacting substances for the course of a chemical change was first clearly established by Wenzel and by Berthollet. The latter pointed out that though under ordinary circumstances sodium carbonate and calcium chloride react almost completely according to the equation



$$Na_2CO_3 + CaCl_2 \rightarrow 2NaCl + CaCO_3,$$

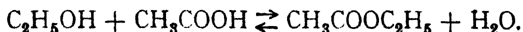
yet the sodium carbonate found on the shores of certain lakes in Egypt is produced according to the equation



$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2,$$

the converse of the first equation. In the latter case, the sodium chloride is present in solution in such large excess that the reaction proceeds in the direction indicated by the arrow, so that, according to Berthollet, an excess in quantity can compensate for a weakness in specific affinity.

An important step forward was made in this subject by Berthelot and Péan de St. Gilles in 1862, in the course of an investigation on the formation of esters from acids and alcohol. For acetic acid and ethyl alcohol, the reaction may be represented by the equation



$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

If one starts with equivalent amounts of acid and alcohol, the reaction proceeds till about 66 per cent. of the reacting substances have been used up, and then comes to a standstill. Similarly, if equivalent quantities of ethyl acetate and water are

heated, the reaction proceeds in the reverse direction (indicated by the lower arrow) until 34 per cent. of the compounds have been used up and the mixture finally obtained is of the same composition as when acid and alcohol are the initial substances. A reaction of this type is termed a *reversible* reaction, and the facts are conveniently represented by the oppositely-directed arrows.

When, however, for a fixed proportion of acid, varying amounts of alcohol are taken, the equilibrium point is greatly altered, as is shown in the accompanying table. The first and third columns show the proportion of alcohol present for 1 equivalent of acetic acid, and the second and fourth columns the proportion of acid per cent. converted to ester.

Equivalents of Alcohol.	Ester Formed.	Equivalents of Alcohol.	Ester Formed.
0·2	19·3	2·0	82·8
0·5	42·0	4·0	88·2
1·0	66·5	12·0	93·2
1·5	77·9	50·0	100·0

We here measure the amount of chemical action by the extent to which the acid is converted into ester, and the table shows very clearly the influence of the mass of the alcohol on the equilibrium.

The influence of the relative proportions of the reacting substances on chemical action was thus clearly recognized, but was not accurately formulated till 1867. In that year, two Norwegian investigators, Guldberg and Waage, enunciated the *Law of mass action*, which may provisionally be expressed as follows: *The amount of chemical action is proportional to the active mass of each of the substances reacting, active mass being defined as the molecular concentration of the reacting substance.* The important part of this statement is that the chemical activity of a substance is not proportional to the quantity present, but to its concentration, or amount in unit volume of the reaction mixture. The law applies in the first instance more particularly to gases and substances in solution; the active mass of solids will be considered later.

The "amount of chemical action" exerted by a certain substance can be measured (*a*) from its influence on the equilibrium, as in the formation of ethyl acetate, just referred to; (*b*) from its influence on the rate of a chemical action, such as the inversion of cane sugar. The law of mass action can therefore be deduced from the results of kinetic or equilibrium experiments. Conversely, once the law is established, it can be employed both for the investigation of rates of reaction and of chemical equilibria, and it is the fundamental law in both these branches of physical chemistry.

In the above form, the law of mass action cannot readily be applied, and it will therefore be formulated mathematically. For purposes of illustration, we choose a reversible reaction between two substances in which only one molecule of each reacts; a typical case is the formation of ethyl acetate and water from ethyl alcohol and acetic acid, already referred to. Calling the molecular concentrations of the reacting substances a and b, the rate at which they combine is, according to the law of mass action, proportional to a and to b separately, and therefore proportional to their product. We may therefore write for the initial velocity of reaction at the time t_0—

$$\text{Rate}_{t_0} \propto ab \text{ or } \text{Rate}_t = kab,$$

where k is a constant—an affinity constant—depending only on the nature of the substances, the temperature, etc. As the reaction proceeds, the active masses gradually diminish, since the original substances are being used up in producing the new substances. If, after an interval of time, t, x equivalents of the ester and water have been formed, the rate of the original reaction will be

$$\text{Rate}_t = k(a - x)(b - x).$$

That this must be so is clear when one bears in mind that a and b represent molecular concentrations, and that for every molecule of ester and of water which are formed, an equal number of molecules of acid and alcohol must be used up. We have now to take into account the fact that the substances formed react to produce the original substances. At the time t, when the concentration of the ester and water is x, the rate

of the reverse reaction will be: $\text{Rate}_t = k_1x^2$, where k_1 is another affinity constant. We then have two reactions proceeding in opposite directions, the velocity of the direct reaction is continually diminishing owing to diminishing concentration, that of the reverse reaction is continually increasing owing to increasing concentration of the reacting substances. A point must ultimately be reached when the velocity of the direct is equal to that of the reverse reaction, and the system will no longer change; this is the condition of equilibrium. If the particular value of x under these conditions is x_1 we have the equations

$$\text{Rate}_{\text{direct}} = k(a - x_1)(b - x_1) \text{ and rate}_{\text{reverse}} = k_1x_1^2,$$

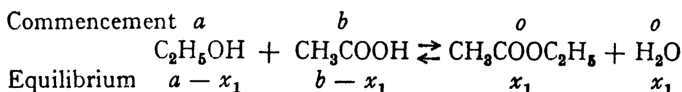
and since these are equal

$$k(a - x_1)(b - x_1) = k_1x_1^2,$$

which may be written

$$\frac{(a - x_1)(b - x_1)}{x_1^2} = \frac{k_1}{k} = \text{K}_c.$$

The facts are made still clearer if we represent the reaction as follows, the initial concentrations being represented on the upper, and the equilibrium concentrations on the lower line:—

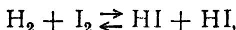


Commencement	a	b	o	o
	C_2H_5OH +	$CH_3COOH \rightleftarrows$	$CH_3COOC_2H_5$ +	H_2O
Equilibrium	$a - x_1$	$b - x_1$	x_1	x_1

It is important to note that, since K_c, which is usually termed the equilibrium constant, is the ratio of the two velocity constants, which are independent of the concentration, the above equation holds for all concentrations. Hence, if the equilibrium constant for any chemical change is obtained from one experiment, the equilibrium conditions can be calculated for any value of the original concentrations. Numerous applications of this equation are given in the succeeding paragraphs.

When more than one molecule equivalent of a compound takes part in a chemical change, *each equivalent must be considered separately*, as far as the law of mass action is concerned.

In order to illustrate this statement, we will consider the combination of hydrogen and iodine to form hydriodic acid. The reaction is reversible, and may therefore be represented by the equation

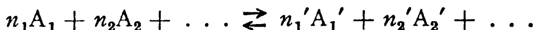


$$H_2 + I_2 \rightleftarrows HI + HI,$$

The rate of the inverse reaction $= k_1 C^2_{HI}$, since it is proportional to the concentration of each of the two mols of hydriodic acid and therefore to their product. As the velocity of the direct reaction $= kC_{H_2}C_{I_2}$, we obtain for the conditions at equilibrium the equation

$$\frac{C_{H_2}C_{I_2}}{C^2_{HI}} = \frac{k_1}{k} = K_c.$$

The general equation for a reversible reaction may be written in the form



$$n_1A_1 + n_2A_2 + \ldots \rightleftarrows n_1'A_1' + n_2'A_2' + \ldots$$

where n_1 molecules of the substance A_1 react with n_2 molecules of the substance A_2 . . . to form n_1' molecules of the substance A_1' and n_2' molecules of the substance A_2'. The rates of the direct and reverse actions are represented by the equations

$$\text{Rate}_{\text{direct}} = kC^{n_1}_{A_1}C^{n_2}_{A_2} \ldots \text{ and rate}_{\text{inverse}} = k_1C^{n_1'}_{A_1'}C^{n_2'}_{A_2'} \ldots$$

and in equilibrium[1]

$$K_c = \frac{k_1}{k} = \frac{C^{n_1}_{A_1}C^{n_2}_{A_2} \ldots}{C^{n_1}_{A_1'}C^{n_2}_{A_2'} \ldots}$$

The above is the strict mathematical form of the law of mass action, which in words may be expressed as follows: *At equilibrium the product of the concentrations on one side, divided by the product of the concentrations on the other side, is constant at constant temperature.* Thus for the reaction represented by the equation $2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2$

$$K_c = \frac{C^2_{FeCl_3}\, C_{SnCl_2}}{C_{SnCl_4}\, C^2_{FeCl_2}}.$$

[1] When the composition of the system is expressed in terms of concentration (mols per litre), the equilibrium constant is written as K_c or simply as K; when partial pressures are used the constant is termed K_p. For the relationship between K_c and K_p, see p. 406

Strict Proof of the Law of Mass Action—The law of mass action, the meaning of which has been illustrated in the previous paragraphs, may be strictly proved by a thermodynamical method (van't Hoff, 1885, *cf.* p. 181), or by a molecular-kinetic method (van't Hoff, 1877). The latter proof is comparatively simple, and depends on the assumption that the rate of chemical change is proportional to the number of collisions between the reacting molecules, which, *in sufficiently dilute solution*, will be proportional to the respective concentrations. Taking again ester formation as an example, the velocity of the direct change $= kC_{alcohol}\ C_{acid}$ and that of the reverse change $= k_1C_{ester}\ C_{water}$. At equilibrium, the rates will just balance, and therefore

$$kC_{alcohol}\ C_{acid} = k_1C_{ester}\ C_{water}.$$

As before, this equation may be put in the form

$$\frac{C_{alcohol}\ C_{acid}}{C_{ester}\ C_{water}} = \frac{k_1}{k} = K,$$

where the respective concentrations are those under equilibrium conditions, and K is the equilibrium constant.

It follows from the assumptions made both in the thermodynamical and kinetic proofs that the law of mass action holds strictly only for very dilute solutions, but the experimental results show that it often holds with a fair degree of accuracy even for moderately concentrated solutions.

Equilibrium in Gaseous Systems. (*a*) **Decomposition of Hydriodic Acid**—A typical example of equilibrium in a gaseous system is that between hydrogen, iodine, and hydriodic acid, investigated by Bodenstein.[1] The reaction, which is represented by the equation $H_2 + I_2 \rightleftarrows 2HI$, is a completely reversible one, the concentration at equilibrium being the same whether one starts with hydrogen and iodine or with hydriodic acid, if the conditions otherwise are the same.

Applying the law of mass action, we get at once

$$\frac{C_{H_2}C_{I_2}}{C^2_{HI}} = K_c \quad . \quad . \quad . \quad . \quad (1)$$

as shown in the previous paragraph.

[1] *Zeitsch. physikal. Chem.*, 1897, **22**, 1.

It is clear from the equation that if from one observation the respective molecular concentrations of iodine, hydrogen, and hydriodic acid are known, K, the equilibrium constant at the temperature in question, can be calculated.

The question now arises as to how the progress of the reaction can be followed, so that it may be known when equilibrium is attained. It is further necessary to find a method of measurement such that the equilibrium does not alter while the observations are being made. In this case it happens that both the direct and inverse reactions are extremely slow at room temperature, but are fairly rapid at 445°, the temperature of boiling sulphur. If then the mixture is heated for a definite time at a high temperature and then cooled rapidly, the respective concentrations at high temperatures can be determined at leisure by analysis. The reacting substances, in varying proportions, are heated at a definite temperature in sealed glass tubes for definite periods, and the amount of hydrogen then present measured after absorption of the iodine and hydriodic acid by means of potassium hydroxide.

For the present, only results will be considered in which the tubes were heated so long at 445° that equilibrium was attained. In one experiment, 20·55 mols of hydrogen were heated with 31·89 mols of iodine, and it was found that the mixture at equilibrium contained 2·06 mols of hydrogen, 13·40 mols of iodine and 36·98 mols of hydriodic acid in the same volume.

Hence $$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{(2{\cdot}06 \times 13{\cdot}40)}{(36{\cdot}98)^2} = 0{\cdot}0200.$$

Equation (1) could, of course, be tested by finding if the same value of K is obtained for different initial concentrations of the reacting substances, but it is in some respects preferable to calculate by means of the equation the proportion of hydriodic acid formed at equilibrium when different initial concentrations of the reacting substances are taken, and to compare the results with those actually observed. In the calculation, K is taken as 0·0200 at 445°.

If 1 mol of hydrogen is heated with a mols of iodine, and $2x$ mols of hydriodic acid are formed, $1 - x$ mols of hydrogen

and $a - x$ mols of iodine will remain behind. Substituting in equation (1),

$$\frac{(1 - x)(a - x)}{4x^2} = K = 0{\cdot}0200 \quad . \quad . \quad (2)$$

The first and second columns of the accompanying table contain the initial concentrations of hydrogen and iodine respectively, and the fourth and fifth columns the observed and calculated concentrations of hydriodic acid at equilibrium, the latter values being obtained from the expression

$$2x = \frac{1 + a - \sqrt{(1 + a)^2 - 4as}}{s}$$

$$\text{where} \quad s = 1 - 4K = 0{\cdot}92$$

obtained by solving the quadratic equation (2) above.

H_2	I_2	$I_2/H_2 = a$	HI found	$2x$ (calc.)
20·57	5·22	0·254	10·22	10·19
20·6	14·45	0·702	25·72	25·54
20·55	31·89	1·552	36·98	37·13
20·41	52·8	2·538	38·68	39·01
20·28	67·24	3·316	39·52	39·25

The close agreement between observed and calculated values shows that the law of mass action applies in this case.

It can easily be shown from the fundamental equation that in this case the position of equilibrium is independent of the pressure or of the volume. Calling a, b, and c the *amounts* of hydrogen, iodine, and hydriodic acid present at equilibrium, the concentrations are a/V, b/V, and c/V respectively, where V is the volume occupied by the mixture. Substituting in the general equation, we obtain $ab/c^2 = K$; in other words, K is independent of the volume. Bodenstein found that this requirement of the theory was also satisfactorily fulfilled.

Equilibrium in Gaseous Systems. (*b*) **Dissociation of Phosphorus Pentachloride**—Another instructive example of equilibrium in a gaseous system is that between phosphorus pentachloride and its products of decomposition, represented by the equation $PCl_3 + Cl_2 \rightleftarrows PCl_5$. A decomposition of this

type, in which a chemical compound yields one or more products, is termed *dissociation*, and the student will have met with many examples of dissociation in his earlier work. As before, on applying the law of mass action, we obtain

$$\frac{C_{PCl_3}C_{Cl_2}}{C_{PCl_5}} = K_c.$$

If we commence with 1 molecule of PCl_5, and x molecules each of PCl_3 and Cl_2 are formed, the concentrations of PCl_5, PCl_3 and Cl_2 at equilibrium are $(1 - x)/V$, x/V, and x/V respectively, and, substituting in the above equation,

$$\frac{x^2}{(1 - x)V} = K_c.$$

It will be observed that the equilibrium in this case depends on the volume, and the larger the volume the smaller is $(1 - x)$ —in other words, the greater is the dissociation.

When, as in the case of phosphorus pentachloride, one molecule of a gas yields n molecules on dissociation the relationship between density and degree of dissociation, x, at constant pressure is as follows: If d_1 is the density and v_1 the volume of the undissociated gas, d_2 the density and v_2 the volume of the partly dissociated gas (in which the number of molecules $(1 - x + nx) = 1 + x(n - 1)$ we have

$$\frac{1}{1 + x(n - 1)} = \frac{v_1}{v_2} = \frac{d_2}{d_1} \text{ whence } x = \frac{d_1 - d_2}{(n - 1)d_2}$$

When the total pressure, P, varies, the equilibrium constant, K_p, when partial pressures are used instead of concentrations, is as follows: When 1 molecule of the gas given 2 molecules on dissociation

$$K_p = \frac{p_{Cl_2}p_{PCl_3}}{p_{PCl_5}} = \frac{\left(\frac{xP}{1 + x}\right)^2}{\frac{(1 - x)P}{1 + x}} = \frac{x^2P}{1 - x^2}.$$

An important point in connection with chemical equilibrium in general is the effect of the addition of excess of one of the products of decomposition (dissociation) on the degree of

decomposition. If, for example, 1 mol of PCl_5 is vaporized in a volume V in which b mols of PCl_3 are already present, and if x_1 is the degree of dissociation of the pentachloride under these conditions, the relative concentrations of trichloride, pentachloride and chlorine will be $b + x_1$, $1 - x_1$, and x_1 respectively. The equilibrium equation is therefore

$$\frac{(x_1)(b + x_1)}{(1 - x_1)V} = K_c,$$

where K_c has the same numerical value as for the pentachloride alone, *provided that the volume* V *and the temperature are the same.* If it is assumed that the degree of dissociation when PCl_5 is heated alone under the same conditions is not more than say 25 per cent., it is clear that the proportion of undissociated compound cannot be very seriously increased by the presence of excess of PCl_3. Hence when b, the initial amount of PCl_3, is made very large, x_1, the amount of chlorine present at equilibrium must become very small in order that the product $K_c\ (a - x_1)$ may retain approximately the same value; in other words, the dissociation of PCl_5 must then be very small. From these considerations we deduce the following important general rule: *The degree of dissociation of a compound is diminished by addition of excess of one of the products of dissociation provided that the volume remains constant.*

Equilibrium in Solutions of Non-Electrolytes—As an illustration of an equilibrium in solution, that between acid, alcohol, ester, and water (p. 162) may be considered rather more fully. For this equilibrium, according to the law of mass action, we have

$$\frac{C_{\text{acid}}\ C_{\text{alcohol}}}{C_{\text{ester}}\ C_{\text{water}}} = K_c.$$

If at the commencement a, b, and c mols of acid, alcohol and water respectively are present in V litres, and under equilibrium conditions x mols of water and ester respectively have been formed, the respective concentrations are

$$C_{\text{acid}} = \frac{a - x}{V};\ C_{\text{alc.}} = \frac{b - x}{V};\ C_{\text{ester}} = \frac{x}{V};\ C_{\text{water}} = \frac{c + x}{V};$$

whence, substituting in the above equation,

$$\frac{(a-x)(b-x)}{x(c+x)} = \mathrm{K}.$$

In this case also, the position of equilibrium is independent of the volume.

The value of K may be obtained from the observation already mentioned, that when acid and alcohol are taken in equivalent proportions, two-thirds is changed to ester and water under equilibrium conditions. Hence

$$\mathrm{K} = \frac{\frac{1}{3} \times \frac{1}{3}}{\frac{2}{3} \times \frac{2}{3}} = \frac{1}{4}.$$

This equation may now be employed, as in the case of hydriodic acid, to calculate the equilibrium conditions for varying initial concentrations of the reacting substances. As an example, we take the proportion of 1 mol of acetic acid converted to ester by varying proportions of alcohol, when the initial mixture contains neither ester nor water. The equation in this case simplifies to

$$\frac{(1-x)(b-x)}{x^2} = \frac{1}{4},$$

whence $x = \frac{2}{3}(1 + b - \sqrt{b^2 - b + 1})$. The observed and calculated values of x are given in the table, and it will be seen that the agreement is very satisfactory, although the solution is so concentrated that it is scarcely to be expected that the law of mass action will apply strictly.

b	x (found)	x (calc.)	b	x (found)	x (calc.)
0·05	0·05	0.049	0·67	0·519	0·528
0·08	0·078	0·078	1·0	0·665	0·667
0·18	0·171	0·171	1·5	0·819	0·785
0·28	0·226	0·232	2·0	0·858	0·845
0·33	0·293	0·311	2·24	0·876	0·864
0·50	0·414	0·423	8·0	0·966	0·945

As regards the practical investigation of this equilibrium, the reacting substances are heated in sealed tubes at constant

temperature (say 100°) till equilibrium is attained, cooled, and the contents titrated with dilute alkali, using phenolphthalein as indicator. As the concentrations of acid and alcohol before the experiment are known and the acid concentration after the attainment of equilibrium is obtained from the results of the titration, the proportion of ester formed can readily be calculated.

The equilibrium in salt solutions will be more conveniently dealt with at a later stage (Chapter XI).

Influence of Temperature and Pressure on Chemical Equilibrium. General—The equations for chemical equilibrium deduced by means of the law of mass action hold for all temperatures provided that all the components remain in the system: the only effect of change of temperature is to alter the value of the equilibrium constant. The displacement of equilibrium is connected with the heat liberated in the chemical change by the equation (*cf.* p. 182)—

$$\frac{d(\log_e K)}{dT} = -\frac{Q}{RT^2} \quad . \quad . \quad . \quad (1)$$

which shows that the rate of change of the logarithm of the equilibrium constant with temperature is equal to the heat evolved in the complete reaction [1] divided by twice the square of the absolute temperature at which the change takes place.

Strictly speaking, the above equation holds only for the displacement of equilibrium due to an infinitely small change of temperature, dT, and must be integrated before it can be applied to a concrete case. This can readily be done on the assumption that Q remains constant between the two temperatures, which is in general only approximately true. Integration between the absolute temperatures T_1 and T_2 gives on this assumption

$$\log_e K_2 - \log_e K_1 = -\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

in which K_1 and K_2 are the equilibrium constants at T_1 and T_2 respectively. When transformed to ordinary logarithms (by

[1] **The negative sign is taken in order that Q may denote the heat evolved in the *forward* reaction (from left to right).**

dividing by 2·3026) and R is put = 1·99 (p. 34), the above equation is obtained in the more convenient form—

$$\log_e K_2 - \log_e K_1 = -\frac{Q}{4\cdot581}\left(\frac{T_2 - T_1}{T_1T_2}\right) \quad . \quad (2)$$

In this equation, Q refers only to the heat used in doing internal work, and does not include that used in external work (p. 145). It applies, therefore, in the first instance, only to systems in which there is no change of volume, and if there is expansion or contraction, the corresponding correction must be applied (p. 149). The equation shows that Q may be calculated when the equilibrium constants for two near temperatures, T_1 and T_2, are known. Conversely, when the heat change in a chemical reaction and the equilibrium constant for any one temperature are known, the condition of equilibrium at any other temperature may be calculated. The equation is particularly useful for the indirect determination of the heat of reaction at high temperatures (in gas reactions, for example) when the direct calorimetric determination is difficult or impossible.

As an example of the application of the general equation (2), the heat of dissociation, Q, for hydrogen sulphide, represented by the equation $2H_2 + S_2 \rightleftarrows 2H_2S$, will be calculated. According to Preuner, the equilibrium constant K of the equation $\frac{[H_2]^2[S_2]}{[H_2S]^2} = K$, has the value $2\cdot90 \times 10^{-5}$ at 1220° abs. and $10\cdot4 \times 10^{-5}$ at 1320° abs. Hence, substituting in equation (2), we have

$$\log_{10}\frac{10\cdot4 \times 10^{-5}}{2\cdot90 \times 10^{-5}} = -\frac{Q}{4\cdot581}\frac{(1320 - 1220)}{(1320 \times 1220)}$$

and Q = − 41,000 cal. approximately.

A specially interesting case is that in which there is no heat change when the first system changes to the second. Since in this case Q = 0, the right-hand side of equation (1) becomes zero, and therefore there should be no displacement of equilibrium with temperature. The condition of zero heat of reaction is, as has already been pointed out (p. 151), approximately fulfilled in ester formation, and in accordance with this, Berthelot

found that at 10° 65·2 per cent. of the acid and alcohol change to ester and at 220° 66·5 per cent.; the displacement of equilibrium with temperature is therefore slight.

There are certain rules of great importance which show qualitatively how the equilibrium is displaced with changes of temperature and pressure. If Q is the heat developed when the system A changes to the system B, and is positive, then with rise of temperature A increases at the expense of B; conversely, if Q is negative, B increases with rise of temperature at the expense of A. These statements may be summarized as follows: *At constant volume increase of temperature favours the system formed under heat absorption and conversely.*

As an example, we may take nitrogen peroxide, $N_2O_4 \rightleftarrows 2NO_2$, for which the change represented by the lower arrow is attended with the liberation of a large amount (12,600 cal.) of heat. Increase of temperature favours the reaction for which heat is absorbed, in this case the reaction represented by the upper arrow, so that as the temperature rises N_2O_4 is split up more completely into NO_2 molecules.

Another interesting example is the relationship between oxygen and ozone, represented by the equation $2O_3 = 3O_2 + 2 \times 29{,}600$ cal. The equilibrium for the reaction $2O_3 \rightleftarrows 3O_2$ is very near the oxygen side at the ordinary temperature, but increase of temperature must displace it in the direction represented by the lower arrow, since under these circumstances heat is absorbed; in other words, ozone becomes increasingly stable as the temperature rises. The experimental results so far obtained are in satisfactory agreement with the theory.[1]

From the above considerations we conclude that endothermic compounds, such as ozone, acetylene, and carbon disulphide, become increasingly stable as the temperature rises, whilst exothermic compounds undergo further dissociation.

[1] Compare Fischer and Marx, *Berichte*, 1907, **40**, 443. At first sight this appears to be in contradiction to the well-known fact that when a mixture of oxygen and ozone is heated to 250° the ozone is practically destroyed. It must be remembered, however, that the mixture contains far too much ozone for equilibrium, but owing to the low temperature it attains its true equilibrium very slowly. At 250°, however, the attainment of equilibrium is fairly rapid.

The same principle applies in connection with the effect of change of temperature on solubility (p. 104).

A similar law can be enunciated for the effect of pressure on equilibrium as follows: *On increasing the pressure at constant temperature the equilibrium is displaced in the direction in which the volume diminishes.* Taking as an illustration the gaseous equilibrium, $PCl_5 \rightleftarrows PCl_3 + Cl_2$, in which the upper arrow indicates the direction of increase of volume, the rule indicates that increase of pressure will displace the equilibrium to the left, whilst decrease of pressure will favour the reverse change. As is well known, these deductions are in complete accord with the experimental facts.

For reactions not attended by any appreciable change of volume, such as the decomposition of hydriodic acid at high temperatures, the equilibrium should not be altered by change of volume, a conclusion borne out by experiment (p. 169).

Le Chatelier's Theorem—Le Chatelier has pointed out that the rules above referred to with regard to the effect of changes of temperature and pressure on equilibria are special cases of a much more general law which may be enunciated as follows: *When one or more of the factors determining an equilibrium are altered, the equilibrium becomes displaced in such a way as to neutralize, as far as possible, the effect of the change.* A little consideration will show that this rule affords a satisfactory interpretation of all the phenomena just mentioned.

Relation between Chemical Equilibrium and Temperature. Nernst's Views—Although the van't Hoff equation connecting equilibrium and temperature enables us to calculate the position of equilibrium at different temperatures when the position of equilibrium at one temperature and the heat of reaction are known, it has not until quite recently been possible to calculate chemical equilibria from thermal and thermochemical data alone. Within the last two or three years, the latter problem appears to have been to a great extent solved by Nernst.[1] The fundamental assumption, on the basis of which it has been found possible to deduce formulæ connecting the equilibrium in a system with the thermal data characteristic of the reacting

[1] Nernst, *Applications of Thermodynamics to Chemistry.* London, Constable, 1907. *Annual Reports, Chemical Society*, 1906, pp. 20-22.

substances, is that the free energy, A, and the total heat of reaction, Q, are not only equal at the absolute zero, as already pointed out (p. 159), but their values coincide completely in the immediate vicinity of that point. It is evident that this assumption cannot be tested directly, but the fact that the formulæ deduced on this basis have been to a great extent confirmed by experiment [1] goes far to justify it.

There can be no doubt that the results just described constitute one of the most important advances in physics and chemistry of recent years. It is beyond the scope of the present book to discuss the question more fully, but it may be mentioned that the theory not only admits of the calculation of equilibria in homogeneous and heterogeneous systems from thermal data, but also gives a formula representing the variation of vapour pressure with temperature.

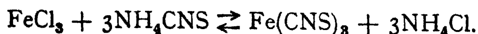
Practical Illustrations—The law of mass action may be illustrated most conveniently by the action of water on bismuth chloride, represented by the equation



$$BiCl_3 + H_2O \rightleftarrows BiOCl + 2HCl.$$

When dilute hydrochloric acid is added to a mixture of the salt and water, the equilibrium is displaced in the direction represented by the lower arrow, and a homogeneous solution is obtained. If excess of water is added to this solution, the equilibrium is displaced in the direction represented by the upper arrow, and a precipitate of bismuth oxychloride is formed.

The law may also be illustrated qualitatively by the interaction of ferric chloride and ammonium thiocyanate to form blood-red ferric thiocyanate.[2] This reaction is of particular interest, as it was one of the first reversible reactions to be systematically investigated (J. H. Gladstone, 1855).[3] The equation representing the reaction is as follows :—



$$FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl.$$

Solutions of the salts are first prepared; the thiocyanate solution contains 3·7 grams of the salt to 100 c.c. of water,

[1] Nernst, *loc. cit.*
[2] Lash Miller and Kenrick, *J. Amer. Chem. Soc.*, **22**, 291.
[3] *Phil. Trans. Roy. Soc.*, 1855, 179.

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and the ferric chloride solution 3 grams of the commercial salt and 12·5 c.c. of concentrated hydrochloric acid to 100 c.c. of water. 5 c.c. of each of the solutions are added to 2 litres of water and the solution divided between four beakers. The solutions are pale-red in colour, as the equilibrium lies considerably towards the left-hand side. To the contents of two of the beakers are added 5 c.c. of the ferric chloride and the thiocyanate solution respectively, and it will be observed that the solutions become deep red, owing to the displacement of the equilibrium in the direction of the upper arrow. On the other hand, the addition of 50 c.c. of a concentrated solution of ammonium chloride[1] to the solution in the third beaker makes it practically colourless, the equilibrium being displaced in the direction of the lower arrow, in accordance with the law of mass action.

APPENDIX

(1) **Application of Second Law of Thermodynamics to Equilibrium between the Different States of Aggregation of a Substance**— The general formula applicable to equilibria of this type will be deduced by means of a reversible cyclic process applied to vaporization—it gives the connection between the latent heat of vaporization and the change of vapour pressure with temperature. According to the second law of thermodynamics, in a reversible cycle

$$\frac{\text{work done}}{\text{heat absorbed}} = \frac{\text{change of temperature}}{\text{temperature of absorption}}.$$

The work done is $(V_2 - V_1)\,dp$, where V_1 is the volume of a mol of substance in the form of liquid, V_2 the corresponding volume in the vapour form and dp is the change of vapour pressure for a small change of temperature dT. Substituting in the above equation, we obtain

$$\frac{(V_2 - V_1)dp}{q} = \frac{dT}{T} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where q is the latent heat of vaporization of 1 mol of liquid at the absolute temperature T.

As the volume of a definite quantity of a substance is so much greater in the vapour than in the liquid form, no great error will be made by neglecting V_1 in comparison with V_2. Further, according to the gas laws (p. 33)

[1] Strictly speaking, all the solutions should be made up to the same volume in each case, but for qualitative purposes the method described is sufficiently accurate. The deep-red colour is presumably due to the formation of non-ionized ferric thiocyanate (p. 266); it cannot be due to $Fe^{\cdots}$ or to CNS^{1} ions, which are practically colourless.

$pV_2 = RT$. Substituting the value of V_2 from this equation in the formula $V_2 dp/q = dT/T$, we obtain

$$\frac{1}{p} \cdot \frac{dp}{dT} = \frac{q}{RT^2}$$

or

$$\frac{d(\log_e p)}{dT} = \frac{q}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The above relationship can be obtained in more convenient form by integration, on the assumption that q remains constant for the small interval of temperature concerned. Integrating between the absolute temperatures T_1 and T_2 (the corresponding pressures being p_1 and p_2) we obtain (*cf.* p. 173)

$$\log_e \frac{p_2}{p_1} = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or

$$\log_{10} p_2 - \log_{10} p_1 = \frac{q}{4{\cdot}581}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \quad . \quad . \quad . \quad (3)$$

As an illustration of the use of formula (3), the value of q for benzene may be calculated from the observation that the vapour pressures at 20° and 30° C. amount to 75·0 mm. and 118 mm. respectively. Hence

$$0{\cdot}19682 = \frac{q}{4{\cdot}581}\left(\frac{10}{293 \times 303}\right)$$

and

$$q = 8004 \text{ calories.}$$

An approximate relationship between latent heat of vaporization and the absolute temperature at which vaporization takes place—the so-called Trouton's rule—states that the quotient of the molecular heat of vaporization by the absolute temperature, is constant—in symbols q/T = constant. The rule is approximately valid for non-associated liquids, but associated liquids, such as water and alcohol, show very considerable deviations.

Formula (1) applies also to other changes of state, for example from solid to liquid. As an illustration the effect of a change of pressure of one atmosphere on the melting-point of ice will be calculated. In all such calculations, care must be taken to state the factors concerned in corresponding units.

The available data are that the latent heat of fusion of ice is 80 calories or 80 × 42,650 gram-cms., that the specific volume of ice is 1·087 when that of water is taken as unit, and that dp is 1033 grams/cm.^{2} Substituting in the equation

$$\frac{(v_2 - v_1)dp}{q} = \frac{dT}{T}$$

we have

$$\frac{0{\cdot}087 \times 1033}{80 \times 42{\cdot}650} = \frac{dT}{273}$$

whence

$$dT = 0{\cdot}0072^\circ$$ (*cf.* p. 191).

It can readily be deduced from the formula that if v_2 is greater than v_1 dp and dT must have the same sign, in other words, increased pressure will raise the melting-point, when, on the other hand, v_2 is less than v_1, as in the case of water, dp and dT are of opposite sign and increase of pressure will lower the temperature at which the transformation occurs.

(2) **Quantitative Measurement of Chemical Affinity**—It has been pointed out (p. 157) that the chemical affinity of a reaction can be measured quantitatively by determining the maximum amount of external work which,

under suitable conditions, the reaction may be made to perform. There are two chief methods in which this principle is applied, (1) by measurement of the position of equilibrium in the system under definite conditions, (2) by means of E.M.F. measurements in a galvanic cell. The second method is fully explained in a later chapter (p. 353), and a proof of the formula used in the equilibrium method and one or two examples will now be given. It will readily be understood that the position of equilibrium must be closely connected with the chemical affinity between the reacting substances since the greater the affinity the more complete will be the combination. It will be sufficient for our present purpose to derive the affinity formula for a reaction in which gases only are concerned; the same formula applies to reactions in heterogeneous systems.

A vessel contains hydrogen, oxygen, and water vapour of the respective concentrations C_{H_2}, C_{O_2}, and C_{H_2O} at the constant temperature T. It is assumed that one of the walls of the vessel is permeable for hydrogen only, another for oxygen only, and a third for water vapour only, and that the walls can be displaced without friction. Outside each of these walls is the particular gas for which it is permeable, at the same temperature and concentration as the corresponding gas inside, and the amounts both outside and inside are so great that no appreciable change in concentration is caused by the passage of a mol of gas into or out of the vessel.

The wall permeable for hydrogen is now moved inwards so that 2 mols of hydrogen are removed from the vessel, and similarly, by moving inwards the wall permeable for oxygen, 1 mol of the latter gas is brought outside. In these processes no work is done, as no alterations of pressure are set up. The hydrogen and oxygen are now allowed to expand reversibly at constant temperature T until they attain any desired smaller concentrations C'_{H_2} and C'_{O_2}. The work done by a mol of a perfect gas in expanding from the volume v to v_1 is

$$A = RT \log_e v_1/v = RT \log_e C/C'$$

and therefore (assuming that both hydrogen and oxygen behave as perfect gases) the total work gained in the above processes is

$$A_1 = 2RT \log_e \frac{C_{H_2}}{C'_{H_2}} + RT \log_e \frac{C_{O_2}}{C'_{O_2}}.$$

The 2 mols of hydrogen (concentration C'_{H_2}) and the mol of oxygen (concentration C'_{O_2}) are now combined to form 2 mols of water vapour of concentration C'_{H_2O}, the latter concentration being so chosen that the water vapour is in equilibrium with hydrogen and oxygen of the respective concentrations C'_{H_2} and C'_{O_2}. No work is done in this combination, which is carried out under equilibrium conditions. Finally the 2 mols of water vapour of concentration C'_{H_2O} are brought isothermally and reversibly to the initial concentration C_{H_2O} and added to the contents of the vessel through the wall permeable for the vapour. In the latter process the work gained is

$$A_2 = 2RT \log_e \frac{C'_{H_2O}}{C_{H_2O}}.$$

The result of these processes is that in the interior of the vessel 2 mols of hydrogen of the concentration C_{H_2} and 1 mol of oxygen of the concentration C_{O_2} have disappeared and 2 mols of water vapour of the concentration C_{H_2O} have been formed without any alteration of temperature or concentration inside the system. The total work gained is

$$A = A_1 + A_2 = 2RT \log_e \frac{C_{H_2}}{C'_{H_2}} + RT \log_e \frac{C_{O_2}}{C'_{O_2}} + 2RT \log_e \frac{C'_{H_2O}}{C_{H_2O}}$$

which is a measure of the affinity of hydrogen and oxygen at the temperature and concentration in question. The above equation may be written in the form

$$A = RT \log_e \frac{C^2_{H_2} C_{O_2}}{C^2_{H_2O}} + RT \log_e \frac{C'^2_{H_2O}}{C'^2_{H_2} C_{O_2}}.$$

Now A depends only on the initial and final states of the system and is therefore independent of the arbitrarily chosen concentrations C'_{H_2} and C'_{O_2} to which the gases were brought after removal from the vessel. It follows that the expression $\frac{C'^2_{H_2O}}{C'^2_{H_2} C'_{O_2}}$ = constant = K, in other words, whatever be the concentrations C'_{H_2} and C'_{O_2}, the concentration C'_{H_2O} of water vapour in equilibrium with C'_{H_2} and C'_{O_2} is such that the above equation holds.

We have here a thermodynamical proof of the law of mass action, first established by Guldberg and Waage from kinetic considerations.

The affinity of hydrogen to oxygen is therefore represented by the formula

$$A = RT \log_e K - RT \log_e \frac{C^2_{H_2O}}{C^2_{H_2} C_{O_2}}$$

and can be obtained for any concentration C of the reacting substances when the equilibrium constant of the action has been determined.

It can easily be shown that a formula of this type applies both to homogeneous and heterogeneous reactions. The general formula is as follows (p. 166) :—

$$A = RT \log_e K - RT \log_e \frac{[A'_1]^{n'_1} [A'_2]^{n'_2} \cdots}{[A_1]^{n_1} [A_2]^{n_2} \cdots}$$

which, when the initial substances and the products are in unit concentration, simplifies to

$$A = RT \log_e K.$$

For the combination of hydrogen and iodine the general formula becomes

$$A = RT \log_e K - RT \log_e \frac{[HI]^2}{[H_2]\,[I_2]}.$$

At the temperature of boiling sulphur ($T = 273 + 445° = 718°$)

$$K = \frac{1}{0{\cdot}02} = 50.$$

The work obtained by the combination of 1 mol of iodine and 1 mol of hydrogen, each at unit concentration, to 2 mols of hydrogen iodide, also at unit concentration, is therefore

$$A = 1{\cdot}985 \times 718 \times 2{\cdot}303 \log_{10} 50 = +\ 5575 \text{ calories}$$

We have here a case where the affinity of a reaction and the heat of reaction are of opposite sign—the latter is about − 6000 cal.

The general formula will now be used to calculate the chemical affinity of a heterogeneous reaction, namely, the maximum work obtainable in the combination of 1 mol of carbon dioxide with calcium oxide at a definite temperature to form calcium carbonate. It is usual to denote the affinity of a gas as that shown towards the solid substances at atmospheric pressure. We proceed to calculate the affinity of carbon dioxide for calcium oxide at 671° C. = 944° abs., the equilibrium pressure at this temperature being 13·5 mm. In this case (p. 184)

$$K = \frac{[CaCO_3]}{[CaO]\,[CO_2]} = \frac{1}{p_{CO_2}}$$

and $A = -\,RT \log_e p.$

therefore $A = -\,1{\cdot}985 \times 944 \times 2{\cdot}303 \log_{10} 13{\cdot}5/760$
$= 7540$ calories.

The value of A obtained is the same whether concentrations or partial pressures are used for calculations in which gases are concerned. In the above calculation the pressure of the atmosphere is taken as unit.

(3) **Deduction of the Formula Connecting Displacement of Equilibrium with change of Temperature.**—Van't Hoff's formula (p. 173) which is usually written in the form

$$\frac{d(\log_e K)}{dT} = \frac{-Q}{RT^2}$$

can easily be deduced from the expression $A - Q = T(dA/dT)$ for the second law of thermodynamics (p. 158) and the affinity formula

$$A = RT \log_e K$$

given in the last section.

From the latter formula we obtain by differentiation

$$\frac{dA}{dT} = R \log_e K + RT\frac{d(\log_e K)}{dT}$$

and $$A - Q = T\frac{dA}{dT} = RT \log_e K + RT^2\frac{d(\log_e K)}{dT}$$

whence $$-Q = RT^2\frac{d(\log_e K)}{dT}$$

or $$\frac{d(\log_e K)}{dT} = \frac{-Q}{RT^2}.$$

CHAPTER VIII

HETEROGENEOUS EQUILIBRIUM. THE PHASE RULE

General—In contrast to homogeneous systems, in which the composition is uniform throughout, heterogeneous systems are made up of matter in different states of aggregation. The separate portions of matter in equilibrium are usually termed *phases;* each phase is itself homogeneous, and is separated by bounding surfaces from the other phases. Liquid water in equilibrium with its vapour is a heterogeneous system made up of two phases, the equilibrium in this case being of a physical nature. Another heterogeneous equilibrium, formed by calcium carbonate with its products of dissociation, consists of three phases, two of which are solid, calcium carbonate and calcium oxide, and one gaseous. A still more complicated case is the equilibrium between a solid salt, its saturated solution and vapour, made up of a solid, a liquid, and a gaseous phase. It should be remembered that though each phase must be homogeneous, both as regards chemical and physical properties, it may be chemically complex. For example, a mixture of gases only forms a single phase, since gases are miscible in all proportions. Further, a phase may be of variable composition, thus a solution only constitutes one phase, although it may vary greatly on concentration.

Application of Law of Mass Action to Heterogeneous Equilibrium—It has already been shown that equilibria in homogeneous systems may be dealt with satisfactorily by means of the law of mass action, *provided that the molecular condition of the reacting substances is known.* The matter is, however, somewhat more complicated for heterogeneous equilibria, more particularly when solid substances are present, as in the equilibrium between calcium carbonate, calcium oxide, and carbon

dioxide already referred to. Debray, who investigated this system very carefully, showed that, just as water at a definite temperature has a definite vapour pressure, independent of the amount of liquid present, there is a definite pressure of carbon dioxide over calcium carbonate and oxide at a definite temperature, independent of the amount or the relative proportions of the solids present. The question now arises as to how the law of mass action is to be applied to systems in which solids are present. This problem was solved by Guldberg and Waage, who found that the experimental results, such as those for the dissociation of calcium carbonate, were satisfactorily represented on the assumption that the *active mass of a solid substance at a definite temperature is constant*, i.e., *independent of the amount of solid present.*

It was not at first clear what physical meaning is to be attached to this statement, but Nernst pointed out that for any such system it was sufficient to consider the equilibrium in the gaseous phase, the active mass of a solid being represented as its concentration in the gaseous phase. In other words, a solid, like a liquid, may be regarded as having a definite vapour pressure at a definite temperature, independent of its amount. At first sight it may seem surprising to ascribe a definite vapour pressure to such a substance as calcium oxide, but it is well known that solids like bismuth and cadmium have definite vapour pressures at moderate temperatures, and there is every reason for supposing that the diminution of vapour pressure with fall of temperature is continuous. There is now no difficulty in applying the law of mass action to equilibria in which solid substances are concerned, for example, to the dissociation of calcium carbonate. For convenience, we will use the partial pressures, p, of the components in the gaseous phase as representing the active masses.[1] We then obtain

$$CaCO_3 \rightleftarrows CaO + CO_2$$

$$kp_{CaCO_3} = k_1 p_{CaO} p_{CO_2},$$

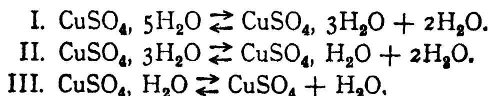
$$\text{whence } p_{CO_2} = \frac{kp_{CaCO_3}}{k_1 p_{CaO}} = \text{constant.}$$

[1] The partial pressure of a gas is proportional to the number of particles present per unit volume and therefore to its molecular concentration or active mass (*cf.* p. 163).

Otherwise expressed, since all the factors on the right-hand side of the equation are constant at constant temperature, the vapour pressure of carbon dioxide must be constant, which is in accordance with the experimental facts.

It is clear from the form of the equation that the pressure remains constant only within limits of temperature such that both calcium carbonate and oxide are present. If the temperature is so high that no calcium carbonate is present, the pressure is no longer defined, but depends on the size of the vessel, etc.

Dissociation of Salt Hydrates—Other interesting examples of heterogeneous equilibrium are those between water vapour and salts with water of crystallization. If, for example, crystallized copper sulphate, $CuSO_4, 5H_2O$ is placed in a desiccator over concentrated sulphuric acid at 50°, it gradually loses water and finally only the anhydrous sulphate remains. If arrangements are made for continuously observing the pressure during dehydration, it will be found to remain constant at 47 mm. until the salt has lost two molecules of water, it then drops to 30 mm. and remains constant until other two molecules of water have been lost, when it suddenly drops to 4·4 mm. and remains constant till dehydration is complete. The explanation of the successive constant pressures observed during dehydration is similar to that already given for the constant pressure of carbon dioxide over calcium carbonate and oxide. At 50° the hydrates $CuSO_4, 5H_2O$ and $CuSO_4, 3H_2O$ are in equilibrium with a pressure of aqueous vapour = 47 mm., and as long as any of the pentahydrate is present, the pressure necessarily remains constant. When, however, all the pentahydrate is used up, the trihydrate begins to dehydrate, giving rise to a little of the monohydrate, $CuSO_4, H_2O$. As a new substance is then taking part in the equilibrium, the pressure of aqueous vapour necessarily alters, and remains at the new value until the trihydrate is used up. The successive equilibria are represented by the following equations :—



I. $CuSO_4, 5H_2O \rightleftarrows CuSO_4, 3H_2O + 2H_2O.$

II. $CuSO_4, 3H_2O \rightleftarrows CuSO_4, H_2O + 2H_2O.$

III. $CuSO_4, H_2O \rightleftarrows CuSO_4 + H_2O.$

By applying the law of mass action to any of the above equations, it may easily be shown that the pressure of aqueous vapour must be constant at constant temperature. Putting the partial pressures of the pentahydrate and the trihydrate as P_1 and P_2 respectively, we have from equation I.—

$$kP_1 = k_1 P_2 p^2_{H_2O}.$$

$$\text{whence } p^2_{H_2O} = \frac{kP_1}{k_1 P_2} = \text{constant.}$$

It is important to realize clearly that the observed pressure is not due to any one hydrate, it is only definite and fixed when both hydrates are present.

The tension of aqueous vapour over hydrates, like the vapour pressure of water, increases rapidly with the temperature. This is illustrated in the following table, in which the vapour pressures (in mm.) over a mixture of Na_2HPO_4, $7H_2O$, and Na_2HPO_4, and those of water at the same temperatures, are given :—

Temperature . .	12·3°	16·3°	20·7°	24·9°	31·5°	36·4°	40·0°
$Na_2HPO_4 + 0 - 7H_2O$	4·8	6·9	9·4	12·9	21·3	30·5	41·2
Water . . .	10·6	13·8	18·1	23·4	34·3	45·1	54·9
Ratio salt/water . .	0·46	0·50	0·52	0·55	0·62	0·68	0·75

The results throw light on the question of the *efflorescence* (giving up of water) and *deliquescence* (absorption of water) of hydrated salts in contact with the atmosphere. If a hydrate (in the presence of the next lower hydrate) has a higher vapour pressure than the ordinary pressure of aqueous vapour in the atmosphere, it will lose water and form a lower hydrate. For example, the salt Na_2HPO_4, $12H_2O$ has a vapour pressure of over 18 mm. at 25°, which is greater than the average pressure of aqueous vapour in the atmosphere at that temperature, though less than the saturation pressure (see table), and therefore the salt is efflorescent under ordinary conditions. On the other hand, the vapour tension of the heptahydrate at 25° is only 13 mm. and it is therefore stable in air. When the vapour pressure of the saturated aqueous solution of a substance is less than the ordinary pressure of aqueous vapour in the atmosphere, the substance will absorb moisture till complete solution occurs; it is said to be *deliquescent*.

Dissociation of Ammonium Hydrosulphide—Solid ammonium hydrosulphide partly dissociates on heating into ammonia and hydrogen sulphide, according to the equation



$$NH_3 + H_2S \rightleftarrows NH_4HS.$$

This equilibrium is of a different type to those already mentioned, as a solid dissociates into two gaseous components. Representing the composition in terms of partial pressures, we obtain, on applying the law of mass action,

$$\frac{p_{NH_3}p_{H_2S}}{p_{NH_4HS}} = K_p, \text{ or } p_{NH_3}p_{H_2S} = K_p p_{NH_4HS} = \text{constant},$$

since the partial pressure of solid ammonium sulphide is constant at constant temperature.

The equation indicates that the product of the partial pressures of the two gases is constant at constant temperature.

When the gases are obtained by heating ammonium hydrosulphide, they are necessarily present in equivalent amount and exert the same partial pressure. The above formula may, however, be tested by adding excess of one of the products of dissociation to the mixture. This was done by Isambert, with the result indicated in the following table, which holds for 25·1°; the volume being kept constant throughout :—

p_{NH_3}	p_{H_2S}	$p_{NH_3}p_{H_2S}$
250·5	250·5	62,750
208·0	294·0	60,700
453·0	143·0	64,800

In the first experiment the gases are present in equivalent proportions, in the second experiment excess of hydrogen sulphide, in the third excess of ammonia have been added. The results indicate that the product of the pressures is constant within the limits of experimental error, as the theory indicates, and, further, that addition of excess of one of the products of dissociation diminishes the amount of the other, as already shown for phosphorous pentachloride (p. 171).

Analogy between Solubility and Dissociation—There is a very close analogy between the solubility of solids in liquids and the

equilibrium phenomena just considered, more particularly the dissociation of salt hydrates. In both cases there is equilibrium between the solid as such and the same substance in the other (gaseous or liquid) phase. We have already seen, in the case of the hydrates of copper sulphate, that the vapour pressure (*i.e.*, the concentration of vapour in the gas space) depends on the composition of the solid phases, and it is then easy to see that the solubility of sodium sulphate (its concentration in the liquid phase) must also depend on the composition of the solid phase. The solubility alters when the solid decahydrate changes to the anhydrous salt, just as does the vapour pressure when copper sulphate pentahydrate disappears. A further analogy between the two phenomena is that just as the addition of an indifferent gas to the gas phase does not alter the equilibrium, except in so far as the volume is changed, so the addition of an indifferent substance to a solution does not greatly affect the solubility of the original solute.

Distribution of a Solute between two Immiscible Liquids—The distribution of a solute such as succinic acid between two immiscible liquids such as ether and water exactly corresponds with the distribution of a substance between the liquid and gas phase (p. 94), and therefore the rules already mentioned for the latter equilibrium apply unchanged to the former. The most important results may be expressed as follows (Nernst):—

(1) If the molecular weight of the solute is the same in both solvents, the *distribution coefficient* (the ratio of the *concentrations* in the two solvents after equilibrium is attained) is constant at constant temperature (Henry's law).

(2) In presence of several solutes, the distribution for each solute separately is the same as if the others were not present (Dalton's law of partial pressures).

The first rule may be illustrated by the results obtained by Nernst for the distribution of succinic acid between ether and water, which are given in the table:—

C_1 (in water)	C_2 (in ether)	C_1/C_2
0·024	0·0046	5·2
0·070	0·013	5·4
0·121	0·022	5·4

The results were obtained by shaking up varying quantities of succinic acid with 10 c.c. of water and 10 c.c. of ether in a separating funnel, and determining the concentrations of acid in the two layers after thay had separated completely. The fact that the ratio C_1/C_2 is approximately constant shows that Henry's law applies.

When the molecular weight of the solute is not the same in both solvents, the ratio of the concentrations is no longer constant, and, conversely, if the ratio of the concentrations is not constant at constant temperature, the molecular weight cannot be the same in both solvents. This is illustrated by the following results obtained by Nernst for the distribution of benzoic acid between water and benzene :—

C_1 (in water)	C_2 (in benzene)	C_1/C_2	$C_1/\sqrt{C_2}$
0·0150	0·242	0·062	0·0305
0·0195	0·412	0·048	0·0304
0·0289	0·970	0·030	0·0293

As the table shows, the ratio C_1/C_2 is not even approximately constant, but, on the other hand, the ratio $C_1/\sqrt{C_2}$ is constant (fourth column). This is connected with the fact that whilst benzoic acid has the normal molecular weight in water, in benzene it is present almost entirely as double molecules (p. 133). According to the general rule there is a constant ratio between the concentrations of the *simple* molecules in the two phases. From the law of mass action the concentration of the simple molecules in benzene is proportional to the square root of the concentration of the double molecules, and, therefore (since the acid is present almost entirely as double molecules), approximately proportional to the square root of the total concentration.

The Phase Rule. Equilibrium between Water, Ice, and Steam—In the previous sections of this chapter it has been shown that many heterogeneous equilibria can be dealt with satisfactorily by means of the law of mass action. This holds not only for phases of constant composition, but within limits also for phases of variable composition, such as solutions. With reference to dilute solutions there is, of course, no difficulty, as the active mass of the solute is proportional to its concentration. This is not the case, however, for concentrated solutions,

and the application of the law of mass action to these is attended with considerable uncertainty.

As far back as 1874, a complete method for the representation of chemical equilibria was developed by the American physicist, Willard Gibbs, which has come to be known as the *phase rule*. The first point to notice with regard to this method is that it is entirely independent of the molecular theory; the composition of a system is determined by the number of *independently variable* constituents, which Gibbs terms *components*. He then goes on to determine the number of "*degrees of freedom*" of a system from the relation between the number of components and the number of phases. It is for this reason that his method of classification is termed the phase rule.

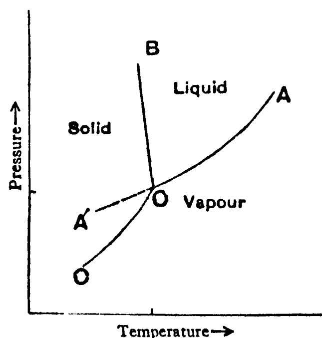


FIG. 25.

In order to make clear the meaning of the terms employed it will be well, before enunciating the rule, to illustrate them by means of a very simple case, namely water. As regards the equilibrium in this case, we may, according to the conditions of the experiment, have one, two or more phases present. Thus, under ordinary conditions of temperature and pressure, there are two phases, water and water vapour, in equilibrium. This equilibrium is represented in Fig. 25 by the line OA, temperature being measured along the horizontal and pressure along the vertical axes. It is only at points on the curve that there is equilibrium. If, for example, at a fixed temperature the pressure is kept *below* that represented by a point on the curve OA (by continuously increasing the volume) the whole of the water will be converted to vapour; if, on the other hand, it is kept at a point a little *above* the curve at a definite temperature, the whole of the vapour will ultimately liquefy. When the temperature is a little below 0°, only ice and vapour are present, and the equilibrium between them is represented on the diagram by the line OC, which is *not* continuous with OA.

The two curves meet at O, and O is the point at which ice and water are in equilibrium with water vapour. It is easy to see that at this point ice and water have the same vapour pressure. If this were not so, vapour would distil from the phase with the higher vapour pressure to that with the lower vapour pressure till the first phase was entirely used up, a result in contradiction with the fact that the two phases remain in equilibrium at this point. Since 0° is the temperature at which ice and water are in equilibrium with their vapour under atmospheric pressure, and as pressure *lowers* the melting-point of ice, the point O, at which the two phases are in equilibrium under the pressure of their own vapour (about 4·6 mm.), must be a little above 0°; the actual value is + 0·007° C. (*cf.* p. 179). The diagram is completed for stable phases by drawing the line OB, which represents the effect of pressure on the melting-point of ice; the line is inclined towards the pressure axis because increased pressure lowers the melting-point.

The point O is termed a *triple point*, because there, and there only, three phases are in equilibrium. At points along the curves two phases are in equilibrium, and under the conditions in the intermediate spaces only one phase is present, as the diagram shows.

So far, only stable conditions have been considered, but unstable conditions may also occur. Thus water does not necessarily freeze at 0°; if dust is carefully excluded, it is possible to follow the vapour pressure curve for some degrees below zero. The part of the curve thus obtained is represented by the dotted line OA′ which is continuous with OA and lies *above* OC, the vapour pressure curve for ice. These results illustrate two important rules: (1) there is no abrupt change in the properties of a liquid at its freezing-point when the solid phase does not separate; (2) the vapour pressure of an unstable phase is greater than that of the stable phase at the same temperature. The last result may be anticipated, since it is then evident how an unstable phase may change to a stable phase by distillation.

The phase rule may now be enunciated as follows: *If* P *represents the number of phases in a system,* C *the number of components, and* F *the number of degrees of freedom, the relation*

between the number of phases, components and degrees of freedom is represented by the equation $C - P + 2 = F$.

The meaning of the terms "component" and "degree of freedom" will become clear as we proceed. The former has already been defined as the smallest number of independent variables of which the system under consideration can be built up. Thus in the case of water, considered above, there is only one component, and the system calcium carbonate-calcium oxide-carbon dioxide can be built up from two components, say calcium oxide and carbon dioxide. Particular instances of the application of the phase rule will now be given.

If the number of phases exceeds the number of components by two, the system has no degrees of freedom ($F = 0$), *and is said to be non-variant.* An illustration of this is the triple point O in the diagram for water (p. 191), where there are three phases (liquid water, ice, and water vapour) and one component (water). If one of the variables, the temperature or the pressure, is altered and kept at the new value, one of the phases disappears; in other words, the system has no degrees of freedom.

If the number of phases exceeds the number of components by one, $F = 1$, *and the system is said to be univariant.* As an illustration, we take the case of water vapour, where there are two phases and one component, say any point on the line OA. In this case the temperature may be altered within limits without altering the number of phases. If the temperature is raised, the pressure will increase correspondingly, and the system will thus adjust itself to another point on the curve OA. Similarly, the pressure may be altered within limits, the system will re-attain to equilibrium by a change of temperature at the new pressure. If, however, the temperature be kept at an arbitrary value and the pressure is then changed, one of the phases will disappear; the system has therefore one, and only one, degree of freedom.

If the number of phases is equal to the number of components, the system has two degrees of freedom, and is said to be divariant. The areas in the diagram (Fig. 25) are examples of this case—there is one phase (vapour, liquid, or solid) and one component. If, for instance, we consider the vapour phase, the temperature may be fixed at any desired point within the triangle AOC, and the pressure may still be altered within limits along a line

parallel to the pressure axis without alteration in the number of phases, as long as the curves OA and OC are not reached.

If the number of phases is less than the number of components by one, the system is trivariant, and so on. This particular instance cannot occur in the case of water, but does so in a four-phase system, as described in the next section.

Equilibrium between Four Phases of the Same Substance. Sulphur—The diagram for water represents the equilibrium between three phases of the same substance. We are now concerned with sulphur, which is somewhat more complicated inasmuch as there are two solid phases, monoclinic and rhombic sulphur, in addition to the usual liquid and vapour phases.

Rhombic sulphur is stable at the ordinary temperature, and on heating rapidly melts at 115°. On being kept for some time in the neighbourhood of 100°, however, it changes completely to monoclinic sulphur, which melts at 120°. Monoclinic sulphur can be kept for an indefinite time at 100° without changing to rhombic; it is therefore the stable phase under these conditions. Thus, just as water is the stable phase above 0° and ice is stable below 0°, there is a temperature above which monoclinic sulphur is stable, below which rhombic sulphur is stable, and at which the two forms are in equilibrium with their vapour. This temperature is termed the *transition point*, and occurs at 95·6°. The change of one form into another is under ordinary conditions comparatively slow, and it is therefore possible to determine the vapour pressure of rhombic sulphur up to its melting-point, and that of monoclinic sulphur below its transition point. Although the vapour pressure of solid sulphur is comparatively small, it has been measured directly down to 50°.

The complete equilibrium diagram, which includes the fixed points just mentioned, is represented in Fig. 26. O is the point at which rhombic and monoclinic sulphur are in equilibrium with sulphur vapour, and is consequently a triple point, analogous to that for water; OB is the vapour-pressure curve of rhombic sulphur, and OA that of monoclinic sulphur. OA′, which is continuous with OA, is the vapour-pressure curve of monoclinic sulphur in the unstable or *metastable* condition; OB′ similarly represents the vapour-pressure curve of rhombic sulphur in the unstable condition, and B′ its melting-point. It will be observed

that in both cases the metastable phase has the higher vapour pressure (p. 191). The line OC represents the effect of pressure on the transition point O and is therefore termed a *transition curve;* since, contrary to the behaviour of water, pressure raises the transition point, the line is inclined away from the pressure axis. Similarly, the curve AC represents the effect of pressure on the melting-point of monoclinic sulphur, and as it is less inclined away from the temperature axis than OC, the two lines meet at C at 131° under a pressure of 400 atmospheres. The

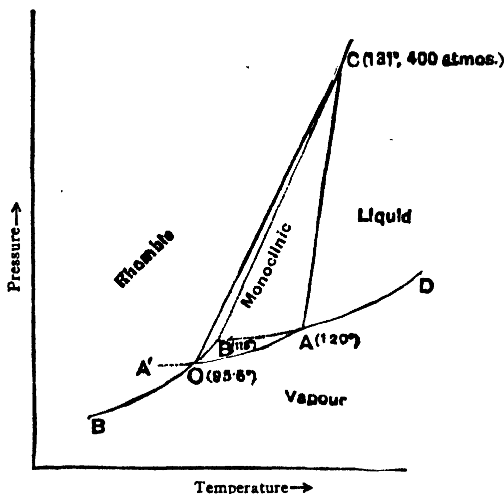


Fig. 26.

curve AD is the vapour-pressure curve of liquid sulphur above 120°, where the liquid is stable, and AB′, continuous with DA, is the vapour-pressure curve of metastable liquid sulphur. As already indicated, B′ represents the melting-point of metastable rhombic sulphur; in other words, it is a *metastable triple point* at which rhombic and liquid sulphur, both in the metastable condition, are in equilibrium with sulphur vapour. OB′, as already indicated, represents the vapour-pressure curve of metastable rhombic sulphur, and the diagram is completed, both for stable and metastable phases, by B′C, which represents the effect

of pressure on the melting-point of rhombic sulphur. Monoclinic sulphur does not exist above the point C; when fused sulphur solidifies at a pressure greater than 400 atmospheres, the rhombic form separates, whilst, as is well known, the monoclinic form first appears on solidification under ordinary pressure. The areas, as before, represent each a single phase, as shown in the diagram. Monoclinic sulphur is of particular interest, because it can only exist in the stable form within certain narrow limits of temperature and pressure, represented in the diagram by OAC.

The phase rule is chiefly of importance in indicating what are the possible equilibrium conditions in a heterogeneous system, and in checking the experimental results. To illustrate this, we will use it to find out what are the possible non-variant systems in the case of sulphur, just considered. From the formula $C - P + 2 = F$, since $C = 1$, P must be three in order that F may be zero; in other words, the system will be non-variant when three phases are present. As any three of the four phases may theoretically be in equilibrium, there must be four triple points, with the following phases:—

(*a*) Rhombic and monoclinic sulphur and vapour (the point O).
(*b*) Rhombic and monoclinic sulphur and liquid (the point C).
(*c*) Rhombic sulphur, liquid and vapour (the point B′).
(*d*) Monoclinic sulphur, liquid and vapour (the point A).

The phase rule gives no information, however, as to whether the triple points indicated can actually be observed. In this particular case they are all attainable, as the diagram shows, but only because the change from rhombic to monoclinic sulphur above the triple point is comparatively slow. If it happened to be rapid, the point B′ could not be actually observed.

Systems of Two Components. Salt and Water—The equilibrium conditions are somewhat more complicated on passing from systems of one component to those of two components, such as a salt and water. For simplicity, the equilibrium between potassium iodide and water will be considered, as the salt does not form hydrates with water under the conditions of the experiment. There will therefore be only four phases, solid salt, solution, ice, and vapour. There are three degrees

of freedom, as, in addition to the temperature and pressure, the *concentration* of the solution may now be varied.

The equilibrium in this system is represented in Fig. 27, the ordinates representing temperatures and the abscissæ concentrations. At 0° (A in the diagram) ice is in equilibrium with water and vapour, as has already been shown. If, now, a little potassium iodide is added to the water, the freezing-point is lowered, in other words, the temperature at which ice and water are in equilibrium is lowered by the addition of a salt, and the greater the proportion of salt present, the lower is the temperature of equilibrium. This is represented on the curve AO, which is the curve along which *ice, solution, and vapour* are in equilibrium. On continued addition of potassium iodide, however, a point must be reached at which the solution is saturated with the salt, and on further addition of potassium iodide, the latter must remain in the solid form in contact with ice and the solution. It is clear that, since the progressive lowering of the freezing-point depends upon the continuous increase in the concentration of the solution, the temperature corresponding with the point O must represent the lowest temperature attainable in this way under stable conditions.

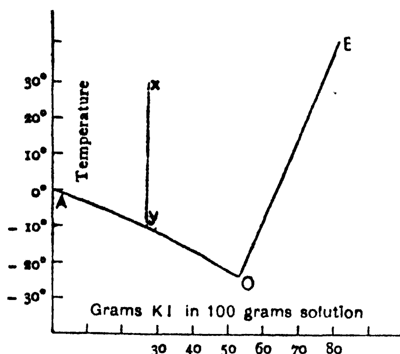


FIG. 27.

To complete the diagram, it is further necessary to determine the equilibrium curve for the solid salt, the solution, and vapour. Looked at in another way, this will be the solubility curve of potassium iodide, which is represented by the curve OB. This curve is only slightly inclined away from the temperature axis, corresponding with the fact that the solubility of potassium iodide only increases slowly with rise of temperature. The point O, which is the lowest temperature attainable with two com-

ponents, is known as a *eutectic point;* in the special case when the two components are a salt and water, it is termed a *cryohydric point.*

The meaning of the diagram will be clearer if we consider what occurs when solutions of varying concentration are progressively cooled. If, for example, we commence with a weak salt solution above its freezing-point (x in the diagram) and continuously withdraw heat, the temperature will fall (along xy) till the line OA is reached; ice will then separate, and as the cooling is continued the solution will become more concentrated and the composition will alter along the line AO until O is reached; salt then separates as well as ice, and the solution will solidify completely at constant temperature, that of the point O. Similarly, if we start with a concentrated salt solution and lower the temperature until it reaches the curve OB, salt will separate and the composition will alter along the curve BO until it reaches the point O, when the mixture solidifies as a whole. Finally, if a mixture corresponding with the composition of the cryohydric mixture is cooled, the line parallel to xy representing the fall of temperature will meet the curve first at the point O, and the mixture will solidify at constant temperature. At the cryohydric temperature, the composition of the solid salt which separates is necessarily the same as that of the solution. Guthrie,[1] who was the first to investigate these phenomena systematically, was of opinion that these mixtures of constant composition were definite hydrates, which were therefore termed *cryohydrates.* At first sight there seems much to be said for this view, as the separation takes place at constant temperature, independent of the initial concentration, and the mixtures are crystalline. For the following reasons, however, it is now accepted that the cryohydrates are not chemical compounds: (*a*) the properties of the mixture (heat of solution, etc.) are the mean of the properties of the constituents, which is seldom the case for a chemical compound; (*b*) the components are not usually present in simple molar proportions; and (*c*) the heterogeneous character of the mixture can be recognized by microscopic examination.

[1] *Phil. Mag.*, 1884, [5], **17**, 462.

The magnitude of the cryohydric temperature is of course conditioned by the effect of the salt in lowering the freezing-point of the solvent, and by its solubility at low temperatures. The eutectic temperatures of solutions of sodium and ammonium chlorides are $- 22°$ and $- 17°$ respectively, that of a solution of calcium chloride $- 37°$.

The application of the phase rule to this system will be readily understood from what has been said above. When there are four phases, ice, salt, solution, and vapour, and two components, we find, by substituting in the formula $C - P + 2 = F$, that $F = 0$, that is, the four phases can only be in equilibrium at a single point, the point O in the diagram. When there are three phases, there is one degree of freedom, and the equilibrium is represented by a line (OA and OB in the diagram). If, for example, the condition of affairs is that represented by a point on the line OA, and the concentration of the solution is increased and kept at the new value (by further addition of salt when necessary) ice will dissolve, and the temperature will fall till it corresponds with that at which ice is in equilibrium with the more concentrated solution and vapour. If, then, while the concentration is still kept at the above value, the temperature is altered and kept at the new value, one of the phases will disappear. The system is therefore univariant. If, instead of the concentration, one of the other variables is changed, corresponding changes in the remaining two variables take place, and the system adjusts itself till the three phases are again in equilibrium.

If there are only two phases, for example, solution and vapour, the phase rule indicates that the system is bivariant, and it can readily be shown, by reasoning analogous to the above, that such is the case.

Freezing Mixtures—The use of mixtures of ice and salt as "freezing mixtures" for obtaining constant low temperatures, depends upon the principles just discussed. Suppose, for example, we begin with a fairly intimate mixture of ice and salt and a little water. When a little of the salt dissolves, the solution is no longer in equilibrium with ice. It will strive towards equilibrium by some more ice dissolving to dilute the solution, the latter, being now more unsaturated with regard

to the salt, will dissolve more of it, more ice will go into solution and so on. As a consequence of these changes, heat must be absorbed in changing ice to water (latent heat of fusion of ice), and in connection with the heat of solution of the salt if, as is usually the case, the heat of solution is negative. The temperature, therefore, falls till the cryohydric point is reached, and then remains constant, since it is under these conditions that ice, salt, solution, and vapour are in equilibrium. As the temperature of a cryohydric mixture is so much below atmospheric temperature, heat will continually be absorbed from the surroundings, but as long as both ice and solid salt are present, the heat will be used up in bringing about the change of state, and the temperature will remain constant. When, however, either ice or salt is used up, the temperature must necessarily begin to rise.

Systems of Two Components. General—The particular case of a two-component or *binary* system already considered—potassium iodide and water—is very simple, for two reasons: (1) the solid phases separate *pure* from the fused mass, in other words, the phases are not miscible in the solid state; (2) the components do not enter into chemical combination. Complications occur when chemical compounds are formed, and when the solid phases separate as *mixed crystals* (p. 106) containing the two components in varying proportions. We will consider three comparatively simple cases of equilibrium in binary systems, the components being in all cases completely miscible in the fused state :—

(*a*) The components do not enter into chemical combination, and are not miscible in the solid state.

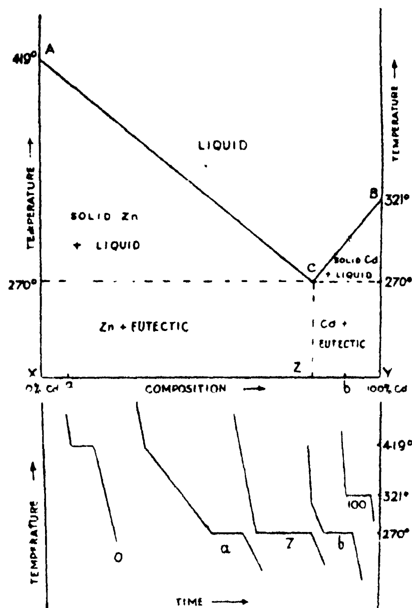
(*b*) The components do not enter into chemical combination, but are completely miscible in the solid state.

(*c*) The components form one chemical compound, but are not miscible with each other or with the compound in the solid state.

Case (*a*). One example of this case is potassium iodide and water which has just been discussed. Another, which will be briefly considered, is the equilibrium between the metals zinc and cadium.[1] To determine the equilibrium curves, mixtures

[1] Hinrichs, *Zeitsch. anorg. Chem.*, 1907, 55, 415.

of these metals in varying proportions are heated above the melting-point, and then allowed to cool slowly, the rate of cooling being observed with a thermocouple, one junction of which is placed in the mixture and the other kept at constant temperature. If the thermocouple is connected to a mirror galvanometer, the rate of cooling can be followed by the movement of a spot of light. Curves in which the times are plotted



Equilibrium Diagram for Zinc and Cadmium.

FIG. 28A (top), 28B (bottom).

against the corresponding temperatures of the mixtures are represented in Fig. 28B. The curves *a*, Z, and *b* represent the cooling of mixtures corresponding with the points *a*, Z, *b* on the composition axis of the upper figure; the curves 0 and 100 represent the cooling of pure zinc and cadmium respectively. For the mixtures there are halts in the rate of cooling—so-called " breaks "—at two points; the first point varies with the composition of the mixture, whilst the second is practically con-

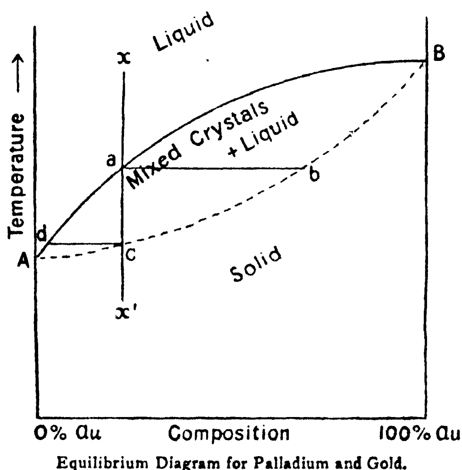
stant at 270°. The curve obtained by plotting the temperatures of the first break against the composition of the mixture is represented in Fig. 28A. The analogy of the diagram with that for potassium iodide and water will be evident, as is its interpretation. The point A represents the freezing-point of zinc, B that of cadmium, the curve AC represents the effect of the gradual addition of cadmium upon the freezing-point of zinc, and BC the effect of zinc in lowering the freezing-point of cadmium, C is the eutectic point at which solid zinc and cadmium are in equilibrium with the fused mass. Consider first a fused mixture rich in zinc. As the temperature falls, a point is ultimately reached at which pure zinc begins to separate, and as the change from liquid to solid is, as usual, attended with liberation of heat, the rate at which the temperature falls will diminish—this represents the first break on cooling. As zinc continues to separate, the composition of the mixture moves along the curve AC, at C the solution is also saturated with regard to cadmium, and therefore at the temperature represented by C, both zinc and cadmium separate in a mixture of the same composition as the fused mass. This, as already mentioned, is the eutectic point, and as the mixture at that point behaves like a single substance, the temperature remains constant till the whole mass has solidified. This is the second break observed when the mixture cools.

If, on the other hand, we commence with a mixture rich in cadmium, the latter separates along the curve BC till the point C is reached, and then the mixture solidifies as a whole. Finally, if a mixture is taken, the composition of which is that of the eutectic mixture, there is only one break in the cooling curve, at the eutectic point (curve Z). The composition of the eutectic mixture is represented by the point Z on the axis of composition XY, and corresponds with 17·4 per cent. of zinc and 82·6 per cent. of cadmium by weight.

Case (*b*). *No chemical compound. Separation of mixed crystals*—A good example of this case is the system palladium-gold,[1] the equilibrium diagram for which is represented in Fig. 29. In this case, when the fused mass is allowed to cool, crystals containing both metals in varying proportions separate,

[1] Ruer, *Zeitsch. anorg. Chem.*, 1906, **51**, 391.

and there is no eutectic point (p. 197). An important rule with regard to such systems is that the concentration of that component by the addition of which the melting-point is lowered is greater in the liquid than in the solid phase; conversely, the concentration of that component by the addition of which the freezing-point is raised is greater in the solid that in the liquid phase. When an alloy of composition x is allowed to cool, it will move down the line xx'. When a is reached crystallization begins, but as the liquid always contains more of the component which lowers the melting-point, the composition of the



Equilibrium Diagram for Palladium and Gold.

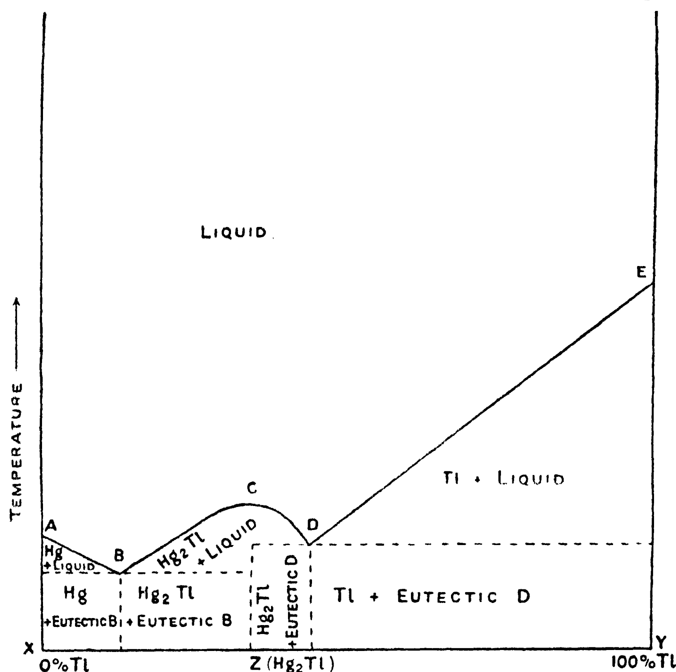
FIG. 29.

crystals separating is represented by b. As freezing continues, the composition of the liquid is represented by a point moving along ad, the solid by points on a second curve bc, to the right of ad. The curve representing the composition of the liquid is called the *liquidus*, that representing the composition of the solid the *solidus*. When the temperature has fallen to c the last of the liquid has solidified and ac is called the *crystallization interval*. As the composition of the liquid from which the solid is separating is continually changing the solid is not homogeneous. The cooling curve of this system shows two breaks

or changes of direction representing the beginning and end of solidification.

Gold and palladium are miscible in all proportions in the solid state, but in many cases the miscibility is limited.

Case (*c*). *One chemical compound. No miscibility in solid form*— A typical freezing-point curve for a system of this type is given



Equilibrium Diagram for Mercury and Thallium.

FIG. 30.

in Fig. 30, representing thallium-mercury amalgams. It will be observed that there is a maximum on the curve, corresponding with the composition of a compound Hg_2Tl, containing two equivalents of mercury to one of thallium. This compound melts at a definite temperature, and it is evident from the curve that the melting-point is lowered both by the addition of

mercury (along CB) and of thallium (along CD). From this it is clear that *the components of a chemical compound lower the freezing-point of the compound just as foreign substances do.* The remainder of the curve will readily be understood from the previous paragraphs. A represents the freezing-point of mercury, AB the lowering of the freezing-point of mercury by the progressive addition of the compound Hg_2Tl, E the melting-point of thallium, and ED the effect on the melting-point of thallium produced by gradually increasing amounts of the same compound. The points B and D are eutectic points, the eutectic mixtures containing mercury and Hg_2Tl, and Hg_2Tl and thallium respectively.

As in Fig. 28, above the curve ABCDE only liquid, and below the dotted line only solid is present. The intermediate regions represent heterogeneous systems in which both liquid and solid are present.

The occurrence of a maximum on the freezing-point curve is usually an indication of chemical combination, but, on the other hand, chemical compounds are sometimes present, although there are no maxima on the curve. This occurs more particularly when the chemical compound decomposes before its melting-point is reached.

The systematic investigation of the freezing-point curve of a binary mixture is one of the best methods for detecting chemical compounds and establishing their formulæ. This can be illustrated by the equilibrium curve of ferric chloride and water, which is of great historical interest, inasmuch as, in the course of the investigation of this system by Roozeboom, many of the points we have been discussing were elucidated.

The Hydrates of Ferric Chloride—The freezing-point curve of this system is represented in Fig. 31, and will be readily understood by comparison with the previous diagrams, more particularly Fig. 30. For convenience, the concentrations in this case are expressed as the ratio of the number of mols of ferric chloride present to 100 mols of water.

In interpreting the curve, we commence at the left-hand side of the diagram. A represents the freezing-point of water, and AB the lowering of freezing-point produced by the progressive

addition of ferric chloride. At the point B, — 55°, the solution is saturated with regard to ferric chloride, and B is therefore the eutectic point, at which ice, solution, a hydrate of ferric chloride (Fe_2Cl_6, $12H_2O$), and vapour are in equilibrium. On adding more ferric chloride, the ice phase will disappear, and equilibrium will be attained at a point on the curve BC, at which the dodecahydrate, Fe_2Cl_6, $12H_2O$, is in equilibrium with solution and vapour. The curve BC may therefore be regarded as the

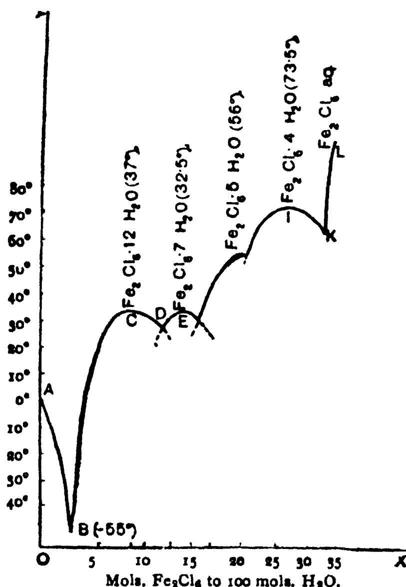


FIG. 31.

solubility curve of the dodecahydrate, and corresponds exactly with the curve OB (Fig. 27). On continued addition of ferric chloride, the equilibrium temperature continues to rise up to the point C at 37°, at which point the composition of the mixture corresponds with that of the dodecahydrate. Further addition of ferric chloride lowers the temperature along the line CD, so that C is a maximum on the curve. At this point, the solid dodecahydrate is in equilibrium with a liquid of the same composition; in other words, C is the melting-point of the compound

$Fe_2Cl_6, 12H_2O$, just as the point C (Fig. 30) represents the melting-point of Hg_2Tl. On addition of more ferric chloride, the melting-point is lowered, as represented by the section CD of the curve. At the point D, the curve reaches another minimum, or eutectic point, which corresponds with the point B, except that a new hydrate, $Fe_2Cl_6, 7H_2O$, takes the place of ice. On further addition of ferric chloride, another maximum is reached, which represents the melting-point of the heptahydrate. In an exactly similar way, the other two maxima at higher concentrations of ferric chloride indicate the existence of two other hydrates, $Fe_2Cl_6, 5H_2O$ and $Fe_2Cl_6, 4H_2O$, in the solid state. At the last eutectic point, K, the four phases in equilibrium are the tetrahydrate, anhydrous ferric chloride, solution and vapour, and KL represents the effect of temperature on the solubility of the anhydrous chloride.

The application of the phase rule to this system should be made by the student. As at the point D (and the other corresponding points) the solubility curves of the dodecahydrate and heptahydrate intersect, D may be termed the *transition point* for the two hydrates. Since at these points there are four phases in equilibrium, they are also termed *quadruple points*.

In recent years, many other systems have been fully investigated on analogous lines to that indicated above. The chief experimental difficulty is to avoid supercooling, a source of error which is much more troublesome in some systems than in others.

Transition Points—In the preceding sections, mention has been made on several occasions of *transition points*. When a substance is polymorphic (*i.e.*, exists in more than one form) it is often possible, as in the case of sulphur, to find a temperature —the so-called transition point—at which two forms are in equilibrium ; at higher temperatures one of the forms is stable, at lower temperatures the other.

It has been shown that at the transition point the two modifications have the same vapour pressure, but at other temperatures the metastable form has the higher vapour pressure. By similar reasoning it can be shown that the metastable phase has the higher solubility and the lower melting-point.

It may happen, however, as in the case of benzophenone, that the modification stable at low temperatures melts before the transition point is reached. It is evident that in this case the transition can only take place in one direction, from the modification the existence of which is favoured by high temperature to that stable at low temperatures. Substances such as sulphur, for which there is a reversible transition, are termed *enantiotropic*, substances for which the transition is only in one direction are termed *monotropic*.

It may be asked how it is possible to obtain the metastable form of benzophenone, as it is necessarily unstable under all conditions. The explanation is that when a fused polymorphic substance is allowed to solidify, it is generally the most unstable form which separates first (*e.g.*, sulphur).

Similarly, the transition point of two hydrates is that temperature at which they are in equilibrium, and at which they have the same solubility and the same vapour pressure.

Practical Illustrations. *Distribution of a solute between two immiscible solvents*—To a nearly saturated aqueous solution of succinic acid (say 100 c.c.) in a stoppered bottle an approximately equal volume of ether is added, and the bottle kept at room temperature for half an hour, shaking it at intervals. When the separation into two layers is complete, part of the ethereal layer is pipetted off and titrated with barium hydroxide, and the same is done with the aqueous layer. Less concentrated solutions of succinic acid are then used, and the concentrations in the ethereal and aqueous layers determined as before. The value of the distribution constant C_1/C_2 is then calculated from the results, and should be constant, as the molecular weight is the same in the two solvents (p. 188).

In a similar way the distribution of benzoic acid between water and benzene may be investigated. In this case, as benzoic acid is unimolecular in water and bimolecular in benzene (p. 189), the ratio $C_1/\sqrt{C_2}$, where C_1 represents the concentration in the aqueous layer, C_2 the concentration in the benzene layer, should be approximately constant.

Determination of transition points—Transition temperatures, such as that above which rhombic sulphur is unstable and monoclinic sulphur stable, can be determined in various ways,

which depend in principle on the difference in properties of the two phases. The dilatometer method is largely used; it is based on the fact that there is a more or less sudden change of volume when the transition takes place. Into a fairly wide glass tube, provided with a capillary tube and scale at the upper end and open at the lower end, is placed a mixture of the two modifications, *e.g.*, monoclinic and rhombic sulphur, the lower end is then sealed up, and the vessel filled to the lower end of the scale with an indifferent liquid such as oil. The dilatometer is then placed in a bath the temperature of which is gradually raised, and readings made of the level of the liquid in the dilatometer. The rate of change of level will be more or less steady till the neighbourhood of the transition point is reached, when a relatively rapid change of level will be observed. The chief drawback to the method is that the change seldom takes place rapidly when the transition point is reached. To facilitate the change as far as possible, some of the second phase should always be present (p. 64).

By solubility or vapour-pressure measurements—The fact that the two phases have the same solubility at the transition point may be employed to determine the latter. To determine the transition point in the system $Na_2SO_4, 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$, it is only necessary to measure the solubility of the anhydrous salt and of the decahydrate in the neighbourhood of the transition point, and the point at which the solubility curves intersect will be the required point.

Measurements of vapour pressure may be employed in a similar way. Thus Ramsay and Young determined the vapour pressures of solid and liquid bromine respectively and found that the curves intersected at $-7°$, which is therefore the transition temperature for solid and liquid bromine; in other words, the melting-point of bromine.

CHAPTER IX

VELOCITY OF REACTION. CATALYSIS

General—In inorganic chemistry, the question as to the rate of a chemical change does not often arise, because in general the reactions are so rapid that it is impossible to measure the speed. The neutralization of an acid by a base, for instance, as shown by the change of colour of the indicator, is practically instantaneous. However, some instances of slow inorganic reactions in homogeneous systems are known. The rate of combination of sulphur dioxide and oxygen to form sulphur trioxide is very slow under ordinary conditions, and the mixture of gases has to be heated in contact with platinum as an accelerating agent in order to obtain a good yield of trioxide. In organic chemistry, on the other hand, slow chemical reactions are very frequently met with. Thus the combination of an organic acid and an alcohol to form an ester is very slow under ordinary conditions, and the mixture of acid and alcohol, saturated with hydrogen chloride, has to be boiled for a considerable time in order to obtain a good yield of ester.

In this chapter, as in the preceding one on chemical equilibrium, the law of mass action is the guiding principle. It has already been pointed out (p. 164) that the rate of a chemical reaction at any instant may be regarded as the difference in the speeds of the direct and the reverse reaction at that instant. If we consider a simple reversible reaction, such as ester formation, in which a, b, c, and d are the initial equivalent concentrations of the reacting substances, and if x is the amount of ester formed in the time t, the equation for the reaction velocity at that instant may be written

$$\frac{dx}{dt} = k(a - x)(b - x) - k_1(c + x)(d + x) \quad . \quad (1)$$

in which dx represents the small increase in the amount of x during the small interval of time, dt. This equation is a direct consequence of the application of the law of mass action to the reaction in question.

It very often happens, however, that the equilibrium lies very near one side, which can only mean that the rate of the reverse reaction is small in comparison with that of the direct reaction. This is clear from the following considerations. The splitting up of hydrogen peroxide into water and oxygen is represented by the equation $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$, and the equilibrium between this compound and its decomposition products by the equation $H_2O_2 \rightleftarrows H_2O + \frac{1}{2}O_2$. Applying the law of mass action, we have

$$k[H_2O_2] \rightleftarrows k_1 [H_2O] [O_2]^{\frac{1}{2}}$$

and

$$\frac{[H_2O_2]}{[H_2O] [O_2]^{\frac{1}{2}}} = \frac{k_1}{k} = K.$$

Now it is an experimental fact that the concentration of hydrogen peroxide in equilibrium with water and oxygen at atmospheric pressure is so small that it cannot be detected by analytical means. It follows, from the above equation, that k_1 is small in comparison with k; otherwise expressed, the rate of the converse reaction, represented by the lower arrow, is negligible in comparison with that of the direct reaction, represented by the upper arrow.

The same considerations apply to the more general case represented by equation (1). If k_1 is negligible in comparison with k, the expression $k_1(c + x)(d + x)$ in equation (1) is negligible in comparison with the remainder of the right-hand side of the equation, and the latter therefore simplifies to

$$\frac{dx}{dt} = k(a - x)(b - x).$$

Reactions of this type, in which the rate of the inverse reaction is negligible, are by far the simplest from a kinetic standpoint, and will therefore be considered first.

Unimolecular Reaction—The simplest type of chemical reaction is that in which only one substance is undergoing change,

and there is practically no back reaction. Such a reaction, which can be readily followed, is the splitting up of hydrogen peroxide to water and oxygen in the presence of colloidal platinum or of certain enzymes. The reaction, which is usually carried out in dilute aqueous solution, may be represented by the equation $H_2O_2 = H_2O + \frac{1}{2}O_2$, and there is the advantage that the solvent does not appreciably alter during the reaction. As the colloidal platinum or the enzyme remains of constant activity during the reaction, the course of reaction is determined solely by the peroxide concentration (*cf.* p. 214).

The reaction in the presence of hæmase (blood-catalase) can conveniently be followed by removing a portion of the solution from time to time, adding to excess of sulphuric acid, which immediately stops the reaction, and titrating with permanganate solution. Some of the results obtained in this way are represented in the accompanying table :—

t (mins.).	$a - x$ (c.c. $KMnO_4$).	x (c.c. $KMnO_4$).	k
0	46·1	0	—
5	37·1	9·0	0·0435
10	29·8	16·3	0·0438
20	19·6	26·5	0·0429
30	12·3	33·8	0·0440
50	5·0	41·1	0·0444

The numbers in the second column represent the number of c.c. of dilute permanganate solution equivalent to 25 c.c. of the reaction mixture when the times represented in the first column have elapsed after mixing the peroxide and enzyme, and therefore represent the concentrations of peroxide in the mixture at the times in question. By subtracting these numbers from that representing the initial concentration of the peroxide, 46·1 c.c., the amounts of peroxide split up at the times t are obtained ; these numbers are given in the third column.

The numbers illustrate very clearly the falling off in the rate of the reaction as the concentration of the peroxide diminishes. Thus in the first ten minutes an amount of peroxide equivalent to 16·3 c.c. of permanganate is split up, whilst in the second interval of ten minutes only 26·5 — 16·3 10·2 c.c. are decomposed.

According to the law of mass action, the rate of the reaction at the time t should be proportional to the concentration of the peroxide, $a - x$, at that time, hence

$$\frac{dx}{dt} = k(a - x) \quad . \quad . \quad . \quad . \quad (2)$$

In this form, however, the equation cannot be applied directly to the experimental results, since dx, the amount of change of x in the time dt, would have to be taken fairly large in order to obtain accurate results, and during the interval $a - x$ would naturally have diminished. Better results would be obtained if $a - x$ were taken as the *average* concentration during the interval dt within which dx of peroxide is being decomposed, but even this method does not give accurate values for k. The difficulty is got over by integrating the equation on principles described in books on higher mathematics. In this way, and bearing in mind that, when $t = 0$, $x = 0$, we obtain from equation (2) above

$$\frac{1}{t} \log_e \frac{a}{a - x} = k \quad . \quad . \quad . \quad (3)$$

It is, however, much more convenient to work with ordinary logarithms (to the base 10) than with logarithms to the base e. Making the transformation in the usual way, we obtain

$$\frac{1}{t} \log_{10} \frac{a}{a - x} = 0{\cdot}4343k \quad . \quad . \quad . \quad (4)$$

By substituting in the above equation corresponding values of a, $a - x$ and t from the table (p. 211), we obtain the values of k given in the fourth column of the table, the average value being 0·0437. Since k is constant within the limits of experimental error, it follows that the assumption on which the equation is based, that the rate of the reaction is proportional to the concentration of the peroxide, is justified.

It is instructive to compare the accurate value of k, obtained by means of the integrated equation (4), with that calculated from the differential equation (2), taking as the value of $a - x$ the average value during an interval. If we choose the interval

between 5 and 10 minutes, $dx = 7{\cdot}3$ c.c., $dt = 5$ minutes, and the mean value of $a - x$ is 33·45 c.c. Hence

$$\frac{7{\cdot}3}{5} = k \times 33{\cdot}45,$$

and $k = 0{\cdot}0436$, which is very close to the accurate average value 0·0437.

A reaction of the above type, in which only one mol of a single substance is undergoing change, is termed a ***unimolecular*** reaction or a reaction of the first order. k is termed the velocity constant, ***and is, for unimolecular reactions, independent of the units in which the concentration is expressed***, but increases considerably with rise of temperature. The meaning of k becomes clear when we consider the initial velocity of the reaction. Under these circumstances, the general equation

$$dx/dt = k(a - x)$$

becomes $dx/dt = ka = 0{\cdot}0437a$ for the example given above. Otherwise expressed, the initial velocity of the reaction = velocity constant × initial concentration. If, by addition of fresh peroxide, the concentration is kept throughout at its initial value, then in unit time (1 minute) 0·0437 of a or over 4 per cent. of a will be decomposed.

If the integrated equation (3) is written in the form

$$\log a/(a - x) = kt,$$

we see that the left-hand side of the equation only becomes infinitely great ($a = x$) when t is infinitely great. Hence, for finite values of t, x is always less than a, in other words, a chemical reaction, even if irreversible, is never quite complete.

Other Unimolecular Reactions—Many unimolecular reactions have been investigated, among the more interesting being the hydrolysis of cane sugar and of esters under the influence of acids. The hydrolysis of cane sugar to dextrose and laevulose is represented by the equation



$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6,$$

and as the acid remains unaltered at the end of the reaction, it does not occur in the equation. The reaction can be conveniently followed by measuring the change in rotation with a polarimeter (p. 75); as cane sugar is dextrorotatory and the mixture of dextrose and laevulose laevorotatory, the rotation diminishes steadily as the reaction progresses, and finally changes sign.

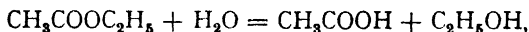
As both sugar and water take part in the reaction, the velocity equation, according to the law of mass action, is

$$\frac{dx}{dt} = kC_{sugar}\,C_{water}.$$

As, however, water is present in great excess, its concentration, and therefore its active mass, remain practically constant throughout the reaction, and the equation therefore reduces to one of the first order, in satisfactory agreement with the experimental results.

Similar considerations enable us to understand why the acid does not appear in the velocity equation. It is true that the rate of the reaction depends upon the concentration of acid present, and this, if necessary, could be expressed by putting in a term C_{acid} on the right-hand side of the velocity equation. But as C_{acid} does not change in the course of the reaction, the only effect is to multiply the right-hand side of the equation by a constant amount which, under ordinary circumstances, we may consider as included in the velocity constant k. In the same way, the enzyme concentration in the example quoted on the previous page is included in the velocity constant, and the course of the reaction is determined by the peroxide concentration.

The hydrolysis of an ester—for example, ethyl acetate—in the presence of excess of a strong acid, such as hydrochloric acid, is represented by the equation



$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH,$$

and is also of the first order, as the active mass of the water is constant. The reaction may readily be followed by removing a portion of the reaction mixture from time to time and titrating with dilute alkali. The measurements may conveniently be

made as follows: To 40 c.c. of 1/2 normal hydrochloric acid previously kept in a 100 c.c. flask for some time at 25°, 2 c.c. of methyl acetate, warmed to the same temperature, is added, the mixture shaken, and the flask well corked and allowed to remain in the thermostat at constant temperature. At first every 20-30 minutes, and then at longer intervals, 2 c.c. of the mixture is removed with a pipette, diluted, and titrated rapidly with N/10 barium hydroxide, using phenolphthalein as indicator. The results are calculated in the usual way by substitution in equation (1). At 25° the value of k for this reaction is 0·0032.

It should be mentioned that it is not necessary to take for the value of a the initial concentration of the reacting substance; the calculation of the velocity constant may be commenced at any stage in the reaction, or may be made from titration to titration. In the latter case the integrated equation for a reaction of the first order is of the form

$$\frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2} = 0{\cdot}4343k$$

where $a - x_1$ and $a - x_2$ are the respective concentrations at the times t_1 and t_2. These methods of calculation gives satisfactory results when, as is not infrequently the case, there are irregularities at the beginning or in the course of a reaction.

Bimolecular Reactions—When two substances react and both alter in concentration, the reaction is said to be bimolecular, or of the second order. If the initial molar concentration of one substance is a that of the other b, and x the amount transformed in the time t, the velocity equation is

$$\frac{dx}{dt} = k(a - x)(b - x) \quad . \quad . \quad . \quad (1)$$

The simplest case is that in which the substances are present in equivalent quantities. The velocity equation then becomes

$$\frac{dx}{dt} = k(a - x)^2,$$

which, on integration, gives the formula

$$\frac{1}{t} \frac{x}{a(a - x)} = k \quad . \quad . \quad . \quad . \quad (2)$$

As an illustration of a bimolecular reaction, the hydrolysis of an ester by alkali may be adduced, a reaction which has been thoroughly investigated by Warder, Ostwald, Arrhenius and others. For ethyl acetate and sodium hydroxide, the equation is as follows :—



$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH.$$

In carrying out an experiment, 1/20 molar solutions of ethyl acetate and of sodium hydroxide are warmed separately in a thermostat at constant temperature (25°) for some time, equal volumes of the solutions are then mixed, and from time to time a portion of the reaction mixture is removed and titrated rapidly with dilute hydrochloric acid. In the following table are given some results obtained by Arrhenius :—

1/50 molar solution at 24·7°.			1/170 molar solution at 24·7°.		
t (min.)	$a - x$	k	t (min.)	$a - x$	k
0	8·04	—	0	2·31	—
4	5·30	0·0160	6	1·87	0·0170
6	4·58	0·0156	12	1·57	0·0170
8	3·91	0·0164	18	1·35	0·0171
10	3·51	0·0160	24	1·20	0·0167
12	3·12	0·0162	30	1·10	0·0163

The numbers for $a - x$ in the second and fifth columns represent the concentrations of sodium hydroxide (and of ethyl acetate) expressed as the number of c.c. of hydrochloric acid required to neutralize 10 c.c. of the reaction mixture. The reaction is very rapid, and therefore the experimental error is somewhat large but the values obtained for k in the third and sixth columns show that the assumptions on which formula (2) is based are justified.

Another bimolecular reaction, which differs from the former inasmuch as two molecules of the same substance react, is the transformation of benzaldehyde to benzoin under the influence of potassium cyanide. The reaction is represented by the equation



$$2C_6H_5CHO = C_6H_5CHOHCOC_6H_5,$$

the potassium cyanide remaining unaltered at the end of the reaction.

When the reacting substances are not present in equivalent proportions, the calculation is somewhat more complicated. On integrating the equation $dx/dt = k(a - x)(b - x)$, we obtain for this case

$$0{\cdot}4343k = \frac{1}{t(a - b)} \log_{10} \frac{b(a - x)}{a(b - x)} \quad . \quad . \quad (3)$$

In order to illustrate the application of this equation, some results obtained by Reicher for the saponification of ethyl acetate by excess of alkali may be adduced. The reaction was followed by titrating portions of the reaction-mixture from time to time with standard acid, as already described, and the excess of alkali was determined by titration of a portion of the solution after the ethyl acetate was completely saponified (at the end of twenty-four hours).

t (min.).	$a - x$ (alkali concentration).	$b - x$ (ester concentration).	k
0	61·95	47·03	—
4·89	50·59	35·67	0·00101
11·36	42·40	27·48	0·00102
29·18	29·35	14·43	0·00103
∞	14·92	0	—

It is important to note that the value of k for a bimolecular reaction is not, as the case of a unimolecular reaction, independent of the units in which the concentration is expressed. If, for example, a unit $1/n$th of the first is chosen, the value of

$$\frac{1}{t} \frac{x}{a(a - x)} \text{ becomes } \frac{1}{t} \frac{nx}{na \,.\, n(a - x)} = \frac{1}{t} \frac{x}{a(a - x)} \cdot \frac{1}{n},$$

so that the value of k diminishes proportionally to the increase of the numbers expressing the concentrations. The truth of this statement can be tested by means of the data for ester saponification due to Arrhenius. If the titrations are made with acid of half the strength actually used ($n = 2$), the numbers expressing the concentrations will be doubled, and it will be found by trial that the value of k becomes half that given in the table.

Trimolecular Reactions—When three equivalents take part in a chemical change, the reaction is termed trimolecular, and several such reactions have been carefully investigated. If, as before, we represent the initial molar concentrations of the reacting substances by a, b, and c respectively, and if x is the proportion of each transformed in the time t, the rate of reaction at that time will, according to the law of mass action, be represented by the differential equation

$$\frac{dx}{dt} = k(a - x)(b - x)(c - x).$$

Such an equation is somewhat difficult to integrate, and we will therefore confine ourselves to the simple case in which the initial concentrations are the same. The equation then becomes $dx/dt = k(a - x)^3$, which on integration gives for k—

$$k = \frac{1}{t}\frac{x(2a - x)}{2a^2(a - x)^2}.$$

Different cases arise according as the reacting molecules are the same or different. The simplest case, in which the three reacting molecules are the same, is illustrated by the condensation of cyanic acid to cyamelide, represented by the equation



$$3HCNO = H_3C_3N_3O_3.$$

A case where two only of the reacting molecules are the same is the reaction between ferric and stannous chlorides, represented by the equation



$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

Finally, the reaction between ferrous chloride, potassium chlorate and hydrochloric acid, represented by the equation



$$6FeCl_2 + KClO_3 + 6HCl = 6FeCl_3 + KCl + 3H_2O,$$

has been shown by Noyes and Wason to be proportional to the respective concentrations of the three reacting substances, and is therefore of the third order.

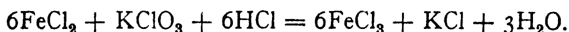
As an illustration of a trimolecular change, some of Noyes' results for the reaction between ferric and stannous chlorides

are given in the table. The reacting substances were mixed together at constant temperature, and from time to time a measured quantity of the solution was removed with a pipette, the stannous chloride decomposed with mercuric chloride, and the ferrous salt still remaining titrated with potassium permanganate in the usual way.

$$SnCl_2 = FeCl_3 = 0{\cdot}0625 \text{ normal} = a.$$

t (min.)	$a - x$	x	k
0	0·0625	0	—
1	0·04816	0·01434	88
3	0·03664	0·02586	81
7	0·02638	0·03612	84
17	0·01784	0·04502	89
25	0·01458	0·04792	89

Reactions of Higher Order. Molecular Kinetic Considerations—Whilst reactions of the first and second order are very numerous, reactions of the third order are comparatively seldom met with, and reactions of a still higher order are practically unknown. This is at first sight surprising, as the equations representing many chemical reactions indicate that a considerable number of molecules take part in the change, and a correspondingly high order of reaction is to be expected. The oxidation of ferrous chloride by potassium chloride in acid solution, for example, is usually represented by the equation



$$6FeCl_2 + KClO_3 + 6HCl = 6FeCl_3 + KCl + 3H_2O.$$

Applying the law of mass action we have therefore

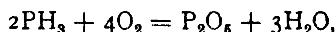
$$\frac{dx}{dt} = k[FeCl_2]^6[KClO_3][HCl]^6,$$

that is, the reaction should be of the thirteenth order, whilst it is actually of the third order (p. 218). To account for this result, it has been suggested by van't Hoff that complicated chemical reactions take place in stages, and that the reaction whose speed is actually measured is one in which only two or three molecules take part, the velocity of the other reactions being very great in comparison. This view is further considered in the next section.

The molecular theory throws a good deal of light on this question. On the assumption that the rate of chemical reaction is proportional to the number of collisions between the reacting molecules (p. 167), it follows that in a trimolecular reaction the three reacting molecules must collide simultaneously to produce a chemical change. The probability of such a collision is extremely small compared with that between two molecules; therefore, if at all possible, the reaction will take place between two molecules or by the change of a single molecule. The probability of the simultaneous collision of four molecules is so small as to be almost negligible.

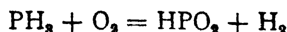
Reactions in Stages—It has just been pointed out that many reactions which are represented by rather complicated equations prove on investigation to be of the second or third order, which seems to show that the reaction, the speed of which is being measured, is in reality a comparatively simple one. When a chemical change takes place in stages, a little consideration shows that it is the *slowest* of a series of reactions which is the determining factor for the observed velocity. This process has been fittingly compared by Walker to the sending of a telegram; the time which elapses between dispatch and receipt is conditioned almost entirely by the time taken by the messenger between receiving-office and destination, as that is by far the slowest in the successive stages of transmission.

An instructive example of a reaction which takes place in stages is the burning of phosphorus hydride in oxygen, investigated in van't Hoff's laboratory by van der Stadt. The change is usually represented by the equation



$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O,$$

according to which it would be a reaction of the sixth order whilst the rate was actually found to be proportional to the respective concentrations of the two gases, the reaction being therefore of the second order. On allowing the gases to mix gradually by diffusion, it was then found that the first stage of the reaction is represented by the equation

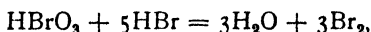


$$PH_3 + O_2 = HPO_2 + H_2$$

—that of a bimolecular reaction—the subsequent changes by

which water and phosphorus pentoxide are produced being very rapid in comparison.

Many other reactions proceed in stages, and in some cases evidence as to the nature of the intermediate compounds has been obtained. Thus the reaction between hydrobromic and bromic acid, usually represented by the equation



$$HBrO_3 + 5HBr = 3H_2O + 3Br_2,$$

is bimolecular in the presence of excess of acid, and it is probable that the first stage (the slow reaction) is as follows :—



$$HBrO_3 + HBr = HBrO + HBrO_2,$$

the subsequent changes, by which bromine and water are finally produced, being comparatively rapid.

It is very probable that the equations which we ordinarily use represent only the initial and final stages in a series of changes, and the determination of the "order" of the reaction is one of the most important methods for elucidating the nature of the relatively unstable intermediate compounds.

Determination of the Order of a Reaction—Three important methods which are largely used in determining the order of reactions may be mentioned here.

(*a*) *The Method of Integration*—According to this method, the values of k given by the integrated equations for reactions of the first, second, and third order are calculated from the experimental results, and the order of the reaction is that in which constant values are obtained for k. The method can be applied to the numbers obtained for the reaction between equivalent amounts of ethyl acetate and sodium hydroxide, when it will be found that the values for k, calculated from the equation $k = 1/t \log a/(a - x)$, continually *decrease* throughout the reaction; the values obtained with an equation of the third order continually *increase*, and only for the equation $k = 1/t \,.\, x/a \,.\, (a - x)$ is k actually constant. The disadvantage of this method is that disturbing causes, such as secondary reactions or the influence of the reaction products on the velocity may so complicate the results that a decision as to the order of the reaction is impossible or an erroneous conclusion may be drawn.

(*b*) *Ostwald's "Isolation" Method*—It has already been

pointed out that if one or more of the reacting substances is taken in great excess, so that their concentration does not alter appreciably during the reaction, the velocity, as far as these substances is concerned, may be regarded as constant. It is on this principle that the "isolation" method is based. Each of the reacting substances in turn is taken in small concentration and all the others in excess, and the relation between the reaction velocity and the concentration of the substance present in small amount determined experimentally. As an example, we will consider the reaction between potassium iodide and iodate in acid solution, investigated by Dushman.[1] Regarding the action of the acid as due to H· ions (p. 134), the reaction velocity, according to the law of mass action, must be represented by the equation

$$\frac{dx}{dt} = k[IO_3']^{n_1}[I']^{n_2}[H^{\cdot}]^{n_3}.$$

When iodide and acid are used in large excess, the velocity is proportional to the iodate concentration ($n_1 = 1$); with a large excess of iodate and acid it is proportional to the square of the iodide concentration ($n_2 = 2$); and finally, when iodide and iodate are in large excess, it is proportional to the square of the acid concentration ($n_3 = 2$). Hence the velocity equation becomes

$$\frac{dx}{dt} = k[IO_3'][I']^2[H^{\cdot}]^2,$$

and when neither of the reagents is present in great excess, is of the fifth order.

(*c*) *Time taken to Complete the same Fraction of the Reaction*—Measurements are made with definite concentrations of the reacting substances, and with double and treble those concentrations, and the times taken to complete a certain stage (say one-third) of the reaction noted. The order of the reaction can then be determined from the following considerations (Ostwald):—

[1] *J. Physical Chem.*, 1904, 8, 453. As the rate of reaction does not depend upon the particular iodate or iodide used, we employ the formulæ for the iodate ion IO_3' and the iodide ion I'.

(1) For a reaction of the first order the time taken to complete a certain fraction of the reaction is independent of the initial concentration.

(2) For a reaction of the second order, the time taken to complete a certain fraction of the reaction is inversely proportional to the initial concentration, *e.g.*, if the concentration is doubled, the time taken to complete a certain fraction of the reaction is halved.

(3) In general, for a reaction of the nth order, the times taken to complete a certain fraction of the reaction are inversely proportional to the $(n - 1)$ power of the initial concentration.

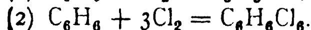
In the experiments by Arrhenius, quoted on page 216, it will be noticed that in the second experiment, in which the concentrations are less than $\frac{1}{3}$ of those in the first experiment, the time taken to complete half the reaction is about three times as long in the former case as in the latter.

Complicated Reaction Velocities—In the present chapter, it has so far been assumed that chemical reactions proceed only in one direction, and are ultimately complete, or practically so, but in many cases these conditions are not fulfilled and the course of the reaction is complicated. The more important disturbing causes are (*a*) side reactions; (*b*) counter reactions; (*c*) consecutive reactions. Each of these will be briefly considered.

(*a*) *Side Reactions*—In this case the same substances react in two (or more) ways with formation of different products; in general the reactions proceed side by side without influencing each other. An example is the action of chlorine on benzene,[1] which may substitute or form an additive product according to the equations



$$(1)\ C_6H_6 + Cl_2 = C_6H_5Cl + HCl,$$



$$(2)\ C_6H_6 + 3Cl_2 = C_6H_6Cl_6.$$

The relative amounts of the products formed in side reactions depend on the conditions of the experiment, and it is usually possible so to choose the conditions that one of the reactions greatly predominates and can be investigated independently.

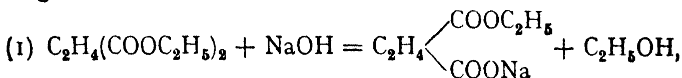
[1] Slator, *Trans. Chem. Soc.*, 1903, **83**, 729.

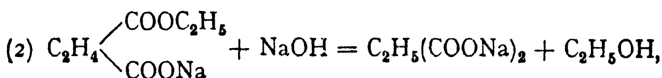
(*b*) *Counter Reactions*—This term is applied when the products of a reaction interact to reproduce the original substances, so that a state of equilibrium is finally reached, all the reacting substances being present (p. 209). Using the same terminology as before, the rate of formation of an ester, for example, will be represented by the differential equation

$$\frac{dx}{dt} = k(a - x)(b - x) - k_1(c + x)(d + x).$$

The conditions can, however, usually be chosen in such a way that either the direct or the reverse reaction predominates, and the values of k and k_1 can thus be determined separately. In this way it has been shown experimentally by Knoblauch[1] that the ratio $k_1/k = K$, the equilibrium constant, as the theory requires (p. 165).

(*c*) *Consecutive Reactions*—Consecutive reactions are those in which the products of a chemical change react with each other or with the original substances to form a new substance or substances. They appear to be of very frequent occurrence (p. 220). A good example is the saponification of ethyl succinate, investigated by Reicher. It proceeds in the following two stages :—





the product of the first reaction, ethyl sodium succinate, reacting further with sodium hydroxide to form the normal sodium salt.

It is important to remember that when one of the reactions is very slow compared with the others, good constants corresponding with the slow reaction are obtained, but when the rates are not very different, the observed velocity does not correspond with any simple order of reaction.

[1] *Zeitsch physikal. Chem.*, 1897, **22**, 268.

CATALYSIS

General—We have already met with instances in which the rate of reaction is greatly increased by the presence of a third substance, which itself is unaltered at the end of the reaction Thus cane sugar is hydrolysed very slowly by water alone, but the change is greatly accelerated by the addition of acids. Such phenomena are termed *catalytic*, and the substance which exerts the catalytic or accelerating action is termed a *catalysor* or *catalyst*. Ostwald, to whom much of our knowledge of catalytic actions is due, defines a catalyst as "a substance which alters the velocity of a reaction, but does not appear in the end products." From the point of view of the quantitative treatment of reaction velocities, it is important to note that the equations already established remain valid in the presence of catalysts, the only effect of the latter being to alter the value of the velocity constant, k. The acceleration produced by a catalyst is in the majority of cases proportional to the amount of the latter added.[1]

Characteristics of Catalytic Actions—From the above it will be seen that the term catalysis does not include any explanation of the observed phenomena; it is merely a classification of reactions which have certain features in common. In order to make clear the exact bearing of the term, some characteristics of catalytic actions will now be adduced.

(*a*) *The catalyst is usually present in relatively small concentration*—This is, of course, connected with the fact that it is not used up during the reaction, so that a relatively small proportion of catalyst can effect the transformation of large amounts of the substance acted on. An apparent contradiction to this rule (as regards the small concentration of the catalyst) is the influence of the medium on the rate of reaction (p. 231), but this can scarcely be termed a true catalytic action.

(*b*) *The catalyst does not start a reaction, but only accelerates a change which can proceed of itself, though perhaps extremely*

[1] One or two exceptions to this rule are known; for example, the accelerating influence of iodine monochloride on the rate of reaction between chlorine and benzene is proportional to the *square* of the concentration of the catalyst (Slator, *Zeitsch. physikal. Chem.*, 1903, **45**, 513).

slowly—Although there is some difference of opinion with regard to the general validity of this statement, it is now fairly widely accepted, and seems to derive support from thermodynamical considerations. As an illustration, we may consider the combination of hydrogen and oxygen to form water. It is well known that the mixed gases can be kept at the ordinary temperature for an almost indefinite time without any apparent combination, but when brought in contact with platinum they combine fairly rapidly. It might at first sight be supposed that the platinum actually initiates the combination. However, when the gases are heated alone at 440°, they combine with a measurable velocity, and at lower temperatures still combination can be observed on long heating. Since the rate of reaction diminishes greatly with fall of temperature (p. 232), it can readily be understood that the rate of combination may be so slow at the ordinary temperature as not to be measurable.

The alternative view is that the hydrogen and oxygen are not entering into combination at all at the ordinary temperature, that they are in a condition of unstable or *false* equilibrium and that the catalyst actually initiates the combination. A direct decision between these alternative hypotheses is difficult, but there is some evidence of the existence of false equilibria. For example, oxygen at fairly low pressures acts readily on phosphorus, but when the pressure reaches a certain value, which depends on the temperature, the reaction stops completely, and there is an apparent equilibrium. The conditions determining this curious phenomenon are not well understood. The limit of pressure above which oxidation does not occur depends on the amount of moisture present, and doubtless also on the presence of traces of impurities.

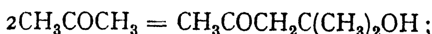
(*c*) *The presence of a catalyst does not affect the equilibrium; it alters the speed of the direct and inverse actions to the same extent*—The truth of the first part of this statement follows at once from the principle of the conservation of energy; provided that the catalyst is not combined with any of the products when the reaction is complete, it does not produce any change in the energy content of the system. It has also been proved experimentally in many cases. Thus Küster found that in the reaction represented by the equation $2SO_2 + O_2 = 2SO_3$, the same equi-

librium point was reached in the presence of such different catalysts as platinum, ferric oxide and vanadium pentoxide.

The second part of the above statement, that the catalyst alters the speed of the direct and inverse actions to the same extent, is a direct consequence of the first part. It has already been shown that the equilibrium constant $K = k_1/k$, so that, if k is increased, k_1 must increase in the same ratio in order that K may remain constant. In accordance with this rule, Baker found that in the complete absence of water vapour, neither of the actions represented by the oppositely-directed arrows in the equation $NH_4Cl \rightleftarrows NH_3 + HCl$ took place, but the presence of moisture accelerated the dissociation of ammonium chloride, as well as its formation from its components.

Examples of Catalytic Action. Technical Importance of Catalysis—There appear to be very few chemical changes which cannot be accelerated by the addition of certain substances, and many catalysts are known. Acids as a class accelerate many chemical changes, more particularly those of hydrolysis, such as the hydrolytic decomposition of cane sugar, of amides, esters, etc., but not of chloroacetic acid.[1] As the catalytic power is in general proportional to the extent to which the acid is split up into its ions, we ascribe the catalytic property to that which is common to all acids, namely, hydrogen ions. Only in dilute solution is there exact proportionality between hydrogen ion concentration and catalytic power. In stronger solutions, for a reason as yet unexplained, the catalytic activity increases more rapidly than the hydrogen ion concentration.

Bases in some cases also exert a catalytic effect, as in the condensation of acetone to diacetonylalcohol, represented by the equation



$$2CH_3COCH_3 = CH_3COCH_2C(CH_3)_2OH\,;$$

in this case the acceleration is proportional to the OH′ ion concentration. Bases have also a powerfully accelerating action in certain isomeric changes of organic compounds.[2]

The rare metals, more particularly finely-divided platinum, also accelerate many chemical reactions, especially oxidation

[1] Senter, *Trans. Chem. Society*, 1907, **91**, 460.

[2] Lowry and Magson, *Trans. Chem. Society*, 1908, **93**, 107.

reactions. Thus platinum is used commercially in the manufacture of sulphuric acid as a catalyst for the reaction $2SO_2 + O_2 = 2SO_3$, as well as in the oxidation of methyl alcohol to formaldehyde and of ammonia to nitric acid. Hydrogen and oxygen also combine to form water at the ordinary temperature in the presence of finely-divided platinum, and the same catalyst also accelerates the splitting up of hydrogen peroxide into water and oxygen. The latter reaction has been investigated fully by Bredig and his pupils, who used the platinum in so-called "colloidal" solution. The solution was obtained by passing the electric arc between platinum poles immersed in cold water; under these circumstances the metal was torn from the poles and remained suspended in the water in a very finely-divided condition (p. 239).

Another interesting catalyst is water vapour. It has been found, for example, that thoroughly dried carbon monoxide does not burn in thoroughly dried air, but when a trace of moisture is present, combination takes place at once. Reference has already been made to the fact that in the complete absence of moisture ammonium chloride can be volatilized without dissociation, and under the same circumstances ammonia and hydrogen chloride do not combine. As the water does not occur in the equation, it acts as a catalytic agent, but its mode of action is quite unknown.

The importance of catalysis for technical processes will be clear from the above. Many important technical reactions are very slow, and the mixture has to be kept for a long period at a high temperature to complete them, which adds much to the cost of production. By using a suitable catalyst, the reaction may be completed at a much lower temperature, and in a much shorter time. As an illustration, the oxidation of naphthalene to phthalic acid by means of sulphuric acid—an important step in the manufacture of indigo—may be referred to. Under ordinary circumstances, the reaction is slow even at high temperatures. Owing to the accidental breaking of a thermometer on one occasion when the reagents were being heated together a little mercury fell into the mixture, and the observation that the reaction then proceeded much more rapidly led to the discovery that mercury was a catalyst for the reaction, and the

whole process was thus rendered commercially successful.[1] The use of copper salts in the Deacon process—production of chlorine by oxidation of hydrogen chloride with free oxygen—and of oxides of nitrogen in the manufacture of sulphuric acid, are other examples of technical catalysis.

Biological Importance of Catalysis. Enzyme Reactions—Catalysis is also of great importance in physiology and allied subjects, as the majority of the changes taking place in the living organism are accelerated by those organic catalysts—the enzymes. When Berzelius brought forward the conception of catalysis, he adduced among other illustrations the hydrolysis of cane sugar by invertase, and the hydrolysis of starch in the presence of an extract of malt. It is now generally recognized that these and allied changes, such as alcoholic fermentation of certain sugars, are due to the action of catalysts of animal or vegetable origin which can be separated from the living cells without losing their activity, and which are termed *enzymes*.

In recent years much progress has been made with the investigation of enzyme reactions, and although little or nothing is known as to the nature of the catalysts themselves, no enzyme having so far been isolated in a state of purity, the laws followed by many enzymes have been satisfactorily elucidated. In general it may be said that enzymes behave like inorganic catalysts, but there are certain characteristic differences. Just as in the case of an inorganic catalyst, the acceleration produced by an enzyme is in the first instance proportional to its concentration. The dependence of the speed of the reaction on the concentration of the substance acted on is, however, not so simple. To take a typical illustration, the rate of hydrolysis of cane sugar in the presence of a constant concentration of invertase increases with the concentration of the sugar in dilute solution, but beyond a certain concentration of sugar, further addition of the latter has no effect on the rate of the reaction. In contrast to this behaviour, the rate of inversion of cane sugar in the presence of a constant concentration of acid increases with the sugar concentration as far as the reaction has been followed.

[1] *Berichte*, 1900, **33**, Appendix.

As in the case of other catalysts, we may expect that the enzyme will accelerate both the direct and inverse actions when the reaction is reversible. The experiments of Croft Hill, Emmerling, Kastle[1] and others, have shown that this expectation is justified.

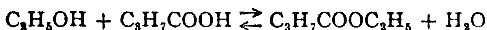
Mechanism of Catalysis—The nature of catalysis becomes somewhat clearer when we represent reaction velocity, in a manner analogous to Ohm's law, by means of the equation

$$\text{Velocity} = \frac{\text{Driving force}}{\text{Resistance}}.$$

The driving force of a chemical reaction is the same thing as the free energy of the system (p. 157); of the resistance little or nothing is known. It is clear from the above equation that the velocity can be altered in two ways, by increasing the driving force and by lessening the resistance. A catalyst cannot to any extent affect the amount of energy in the system, and we must therefore assume that in some way it increases the velocity by diminishing the resistance. Ostwald compares the action of a catalyst to that of oil on a machine, and it is evident that the analogy is far-reaching.

It may be asked whether all catalytic accelerations are due to a common cause. This is very unlikely; it is much more probable that the mechanism of the acceleration varies with the nature of the catalyst and with that of the reacting substances. The suggestion of Liebig, that the catalyst sets up certain molecular vibrations which lead to chemical changes, has proved quite unfruitful. So-called explanations of this nature, though often employed even at the present day, are bad in principle, as we know very little of the nature of molecular vibrations. It is, however, quite justifiable to inquire into the mechanism of catalytic actions, in so far as it can be elucidated

[1] Kastle and Loevenhart have shown that the reactions represented by the upper and lower arrows in the equation

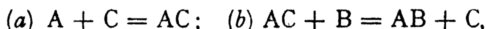


$$C_2H_5OH + C_3H_7COOH \rightleftarrows C_3H_7COOC_2H_5 + H_2O$$

(formation and hydrolysis of ethyl butyrate) are both accelerated by lipase, the enzyme which effects the hydrolysis of fats (*Amer. Chem. J.*, 1900, **24**, 491).

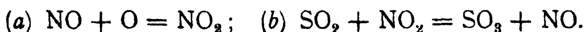
by experimental investigation, and in recent years some light has been thrown on this subject.

An explanation of catalytic acceleration which is much favoured is that it depends on the formation of intermediate compounds of the catalyst with the reacting substances. A reaction represented by the equation $A + B = AB$ may proceed very slowly directly, but in the presence of a catalyst C it may proceed in the following two stages:—



$$(a)\ A + C = AC; \quad (b)\ AC + B = AB + C,$$

much more rapidly to the same final products. For example, it is known that the reaction $SO_2 + O = SO_3$ is a slow one, and the accelerating effect of nitric oxide on the combination may be represented in the following stages:—



$$(a)\ NO + O = NO_2; \quad (b)\ SO_2 + NO_2 = SO_3 + NO.$$

This explanation of the action of the oxides of nitrogen was suggested more than a century ago by Clement and Desormes, and remains the most plausible one at the present day. It is possible that the finely-divided metals act as catalytic agents mainly in a physical manner. In virtue of their large surface, these metals condense gases and to some extent dissolved substances, and the local increase of concentration thus produced must greatly increase the rate of chemical change. Similar considerations may explain the catalytic effect of certain enzymes. A chemical explanation of the action of finely-divided metals and of enzymes—based on the formation of intermediate compounds—is, however, to be preferred.

Nature of the Medium—The rate of a chemical change depends greatly on the nature of the medium in which it takes place, but the way in which the influence is exerted is quite unknown. The most complete data on this subject are due to Menschutkin, who determined the rate of combination of triethylamine and ethyl iodide, represented by the equation



$$(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4NI$$

in more than twenty solvents at 100°. A few typical results are given in the accompanying table, in which k, as usual, represents the velocity constant:—

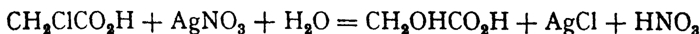
Solvent.	*k*.	Dielectric Constant
Hexane . .	0·00018	1·86 (12·3°)
Ethyl ether . .	0·000757	4·36 (18°)
Benzene . .	0·00584	2·26 (19°)
Ethyl alcohol .	0·0366	21·7 (15°)
Methyl alcohol .	0·0516	32·5 (16°)
Acetone . .	0·0608	21·8 (15°)

It will be seen that the rate varies enormously with change of medium; thus the ratio of the velocities in hexane and acetone is approximately 1 : 340.

It is interesting to inquire whether there is any other property of the different media which is parallel to the effect on the reaction velocity. It was suggested on theoretical grounds by J. J. Thomson, and somewhat later by Nernst, that the "dissociating power of the medium" must be greater the higher its specific inductive capacity or, to use the more modern term, its dielectric constant. The dielectric constants of the media are given in the third column of the table, and it will be seen that there is a distinct parallelism, though not direct proportionality, between dielectric constant and reaction velocity. This question will be again referred to at a later stage.

Even a small change in the medium has sometimes a remarkable effect on the rate of reaction. Thus it has recently been shown that the rate of reaction between pure sulphuric acid and oxalic acid is reduced to 1/17 of its original value by the addition of 0·1 per cent. of water to the reaction mixture.

On the other hand, a considerable alteration in the medium may have very little effect on the velocity. Thus the rate of reaction between chloracetic acid and silver nitrate, represented by the equation

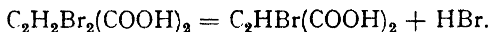


$$CH_2ClCO_2H + AgNO_3 + H_2O = CH_2OHCO_2H + AgCl + HNO_3$$

is practically the same in water and in 45 per cent. alcohol.

Influence of Temperature on the Rate of Chemical Reaction—It is a matter of common experience that the rate of chemical reactions is greatly increased by rise of temperature. Thus the combination of hydrogen and oxygen is so slow at the ordinary temperature that it cannot be detected (p. 226), but

at high temperatures it proceeds with explosive rapidity. It has already been pointed out that rise of temperature does not usually affect the form of the velocity equation; it can be represented simply as altering the magnitude of the velocity constant. The more important facts in this connection are well illustrated in the following table, which represents the effect of temperature on the magnitude of the velocity constant for the unimolecular reaction between dibromosuccinic acid and water, represented by the equation



$$C_2H_2Br_2(COOH)_2 = C_2HBr(COOH)_2 + HBr.$$

Temperature.	k (time in minutes).	Temperature.	k (time in minutes).
15°	0·00000967	70·1°	0·00169
40°	0·0000863	80·0°	0·0046
50°	0·000249	89·4°	0·0156
60·2°	0·000654	101·0°	0·0318

The table shows (1) that the velocity increases enormously with rise of temperature; at 15° and 101° the relative rates are in the ratio 0·00000967 : 0·0318 or 1 : 3300; (2) the ratio for a rise of 10° is approximately the same at different temperatures, thus $k_{80}/k_{70} = 2·72$, $k_{50}/k_{40} = 2·88$. It is important to remember that the rate of most chemical reactions, as in the above example, is doubled or trebled for a rise of 10°. This is shown in the accompanying table, which gives the quotient for 10° $(k_{t+10°}/k_t)$ for a few typical chemical reactions.[1]

[1] The third column contains the average value of the quotient for 10° between the temperatures of observation. As data are not always available at intervals of 10°, the average value of $k_{t+10°}/k_t$ may be calculated approximately from the equation

$$\log_{10}k_2 - \log_{10}k_1 = A(T_2 - T_1)$$

where k_1 and k_2 are the velocity constants at the temperatures T_1 and T_2 respectively. (See next section.) This equation gives us the value of A, and the quotient for 10° is given by

$$\log_{10}(k_{t+10})/k_t = 10A \text{ or } \frac{k_{t+10}}{k_t} = 10^{10A}$$

As an example, we will work out the quotient for 10° for the inversion of cane sugar from the data given in the table. $\log_{10} 35·5 - \log_{10} 0·765$ is 1·66657 and as $T_2 - T_1 = 30°$ we obtain A = 0·05555. Hence

$$\log_{10}(k_{t+10})/k_t = 0·5555 \text{ and } (k_{t+10})/k_t = 3·60 \text{ approximately.}$$

Reaction.	Velocity Constants.		Quotient for 10°.
$AsH_3 = As + 3H$ . .	$k_{256} = 0{\cdot}00035$	$k_{367} = 0{\cdot}0034$	1·23
$2NO = N_2 + O_2$ . .	$k_{689} = 39{\cdot}63$	$k_{1347} = 191800$	1·17
$CH_3COOC_2H_5 + NaOH$	$k_{9{\cdot}4} = 2{\cdot}307$	$k_{44{\cdot}90} = 21{\cdot}648$	1·89
$CH_2ClCOONa + NaOH$	$k_{70} = 0{\cdot}00089$	$k_{102} = 0{\cdot}015$	2·5
$CH_2ClCOONa + H_2O$.	$k_{70} = 0{\cdot}000042$	$k_{10} = 0{\cdot}00170$	3·2
$C_2H_5ONa + CH_3I$.	$k_0 = 0{\cdot}00336$	$k_{30} = 2{\cdot}125$	3·34
Inversion of cane sugar .	$k_{25} = 0{\cdot}765$	$k_{55} = 35{\cdot}5$	3·6
$H_2O_2 = H_2O + O$ . .	$k_0 = 0{\cdot}0120$	$k_{10} = 0{\cdot}0180$	1·5
Fermentation by yeast .	10-20°	—	3·8
" " .	30-40°	—	1·6

The quotient for 10° for reactions in solvents other than water is also between 2 and 3 in the majority of cases.

According to the molecular theory, rise of temperature ought to increase the rate of chemical change, owing to the accelerating effect on molecular movements. This effect, however, would only increase proportionally to the square root of the absolute temperature (p. 38), and it can easily be calculated on this basis that the quotient for 10° for a bimolecular reaction at the ordinary temperature would be about 1·04, much too small to account for the large temperature coefficient actually observed. Up to the present, no plausible explanation of the great magnitude of the temperature coefficient of chemical reactions has been given. The only other property which appears to increase as rapidly with temperature is the vapour pressure, and it is not improbable that there is a close connection between vapour pressure and chemical reactivity.

At moderate temperatures the temperature coefficients of enzyme reactions are approximately the same as those of chemical reactions in general, but at temperatures in the neighbourhood of 0°, the rate of change of k with the temperature is often abnormally high, as the table shows.

It is interesting to note that the rate of development of organisms, for example, the rate of growth of yeast cells, the rate of germination of certain seeds, and the rate of development of the eggs of fish, is also doubled or trebled for a rise of temperature of 10°, and it has therefore been suggested that these processes are mainly chemical.

Formulæ connecting Reaction Velocity and Temperature—As has already been pointed out (p. 173), the law connecting the displacement of equilibrium with temperature is known. So far, however, no thoroughly satisfactory formula showing the relationship of rate of reaction and temperature has been established, although many more or less satisfactory empirical formulæ have been suggested. If the relationship which has been shown to hold approximately for the rate of decomposition of dibromosuccinic acid—that the quotient for 10° is the same at high as at low temperatures—holds in general, the equation connecting k and T must be of the form

$$d(\log_e k)/dT = A$$

where A is constant. On integration, this becomes

$$\log k = AT + B,$$

B being a second constant. This formula holds for the decomposition of nitric oxide and for certain other reactions, but is not generally valid. As a matter of fact, the quotient k_{t+10}/k_t generally diminishes with rise of temperature. An equation which takes account of this has been proposed by Arrhenius; in its integrated form the equation is as follows:—

$$\log k = -A/T + B.$$

For two temperatures, T_1 and T_2, for which the values of the velocity constant are k_1 and k_2 respectively, the above equation becomes

$$\log_e k_2 - \log_e k_1 = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

and when A is known (from two observations) the velocity constant for any other temperature can be calculated.

Arrhenius showed that the above empirical equation represents satisfactorily the influence of temperature on the rate of hydrolysis of cane sugar and on certain other reactions, and it has since been employed by many other observers with fairly satisfactory results. A is a constant for any one reaction, but differs for different reactions.

Practical Illustrations—As the rate of chemical reactions alters so greatly with change of temperature, it is necessary in accurate experiments to work in a thermostat provided with a regulator to keep the temperature constant. For purposes of illustration, however, sufficiently accurate results can be obtained by using so large a volume of solution that the temperature does not alter appreciably during the reaction.

Unimolecular Reaction. (*a*) *Decomposition of Hydrogen Peroxide*[1]—To 200 c.c. of a mixture of one part of defibrinated ox-blood and 10,000 parts of water, an equal volume of about 1/100 molar hydrogen peroxide (0·34 gram per litre) is added, and the mixture shaken. At first every ten minutes, and then at longer intervals, 25 c.c. of the reaction mixture is removed with a pipette, added to a little sulphuric acid, which at once stops the action, and titrated with 1/100 normal potassium permanganate. If pure hydrogen peroxide is not available, the commercial product should be neutralized with sodium hydroxide before use.

Another portion of the original hydrogen peroxide solution should be titrated with permanganate, and if the reacting solutions have been measured carefully, the initial concentration in the reaction mixture may be taken as half that in the original solution.

The observations should be calculated by substitution in the formula $1/t \log a/a - x = 0{\cdot}4343\,k$, valid for a unimolecular reaction.

A corresponding experiment may be made with double the peroxide concentration, in order to illustrate the fact that the time taken to complete a certain fraction of the reaction is independent of the initial concentration.

(*b*) *Hydrolytic Decomposition of Cane Sugar in the Presence of Acids*—Equal volumes of a 20 per cent. solution of cane sugar and of normal hydrochloric acid, previously warmed to 25°, are mixed, the observation tube of a polarimeter is filled with the mixture, and an observation of the rotation taken as quickly as possible. The polarimeter tube is then immersed

[1] Senter, *Zeitsch. physikal. Chem.*, 1903, **44**, 257. The amount of organic matter is so small that the error in titration due to its reducing action on permanganate is negligible.

in a thermostat at 25°, and kept in the latter except when readings of the rotation are being made. In order that it may be conveniently immersed in a thermostat, the polarimeter tube is provided with a side tube, through which it is filled, and the end of which is not immersed. To prevent alterations while readings are being made, the tube is provided with a jacket filled with water at the temperature of the thermostat.

Several chemists have described arrangements according to which the tube remains in the polarimeter throughout an experiment, the temperature being kept constant by passing a stream of water at constant temperature through the jacket of the polarimeter tube.[1] With rapid working, however, the simpler method described above gives excellent results.

If it is convenient to make an observation after the reaction is complete (say 24 hours), the total change of reading is taken as a in the formula for a unimolecular reaction, and the difference of the initial reading and that of the time, t, is proportional to x, the amount of sugar split up. If the reaction is not complete in a reasonable time, the final reading can be calculated from the fact that for every degree of rotation to the right in the original mixture, the wholly inverted mixture will rotate 0·315° to the left at 25°.

(*c*) *Hydrolysis of Ethyl Acetate in the Presence of Hydrochloric Acid*—The method of experiment in this case has already been described (p. 215).

Bimolecular Reaction. (*a*) *The rate of reaction is proportional to the concentration of each of the reacting substances*—This statement can be illustrated very satisfactorily by a method described by Noyes and Blanchard, and depending upon the fact that the time taken to reach a certain stage of a reaction is inversely proportional to its rate.

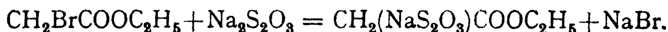
In a two-litre flask a mixture of 1600 c.c. of water, 50 c.c. half-normal hydrochloric acid and 20-30 c.c. of dilute mucilage of starch is prepared, and 400 c.c. of this mixture is placed in each of 4 half-litre flasks of clear glass, standing on white paper. For comparison, a fifth half-litre flask contains 400 c.c. of water, 10 c.c. of starch solution, and sufficient of a $n/100$ solution of iodine to give a blue colour of moderate depth.

[1] *Cf.* Lowry, *Trans Faraday. Society*, 1907, **3**, 119.

Half-normal solutions of potassium bromate (7 grams per half-litre) and of potassium iodide are also prepared. To the flasks I. and II. 5 c.c. of the bromate solution is added, and to III. and IV. 10 c.c. of the same solution. Then at a definite time, 5 c.c. of the iodide solution is added to flask I., the mixture rapidly shaken, and the time which elapses until the solution has the same depth as the test solution carefully noted. Then to flasks II., III., and IV. are added successively 10 c.c., 5 c.c., and 10 c.c. of the iodide solution, and the times required to attain the same depth of colour as the test solution carefully noted in each case. If x is the time required when 10 c.c. of each reagent is used, $2x$ will be the time required when 10 c.c. of one solution and 5 c.c. of the other is used, and $4x$ when 5 c.c. of each solution is used.

If for some reason the reactions are too rapid, the strengths of the bromate and iodide solutions should be altered till intervals convenient for measurement are observed.

(*b*) *Quantitative measurement of a bimolecular reaction*—The rate of reaction between ethyl acetate and sodium hydroxide may be measured as described on a previous page. From a practical point of view, however, the measurement presents certain drawbacks because it is difficult to prepare a solution of sodium hydroxide free from carbonate and also to prevent absorption of that gas from the air during the experiment. A reaction [1] free from these disadvantages, which is very rapid in dilute solution, is that between ethyl bromoacetate and sodium thiosulphate, represented by the equation



$$CH_2BrCOOC_2H_5 + Na_2S_2O_3 = CH_2(NaS_2O_3)COOC_2H_5 + NaBr.$$

The rate of the reaction can readily be followed by removing a portion of the reaction mixture from time to time and titrating with $n/100$ iodine, which reacts only with the unaltered thiosulphate.

300 c.c. of an approximately 1/60 normal solution of sodium thiosulphate is added to an equal volume of a dilute aqueous solution of ethyl bromoacetate (2·2·1 grams per litre) in a litre flask, the mixture shaken and the flask closed by a cork.

[1] Slator, *Trans. Chem. Society*, 1905, 87, 484.

At first every 5 minutes, and then every 10 or 15 minutes, 50 c.c. of the reaction mixture is removed with a pipette and titrated rapidly with $n/100$ iodine, using starch as indicator. Seven or eight such titrations are made, and then, after an interval of 5-6 hours, when the reaction is presumably complete, a final titration is made in order to determine the excess of thiosulphate remaining. The initial concentration of thiosulphate, expressed in c.c. of the iodine used in titrating the mixture, can be obtained by titrating part of the original thiosulphate solution, and the initial concentration of bromoacetate in the reaction-mixture is clearly equivalent to the amount of thiosulphate used up. The case is exactly analogous to that quoted on page 217, in which the sodium hydroxide is in excess, and the value of k may be obtained by substitution in equation (3), p. 217.

Catalytic Actions—The decomposition of hydrogen peroxide by blood and of cane sugar in the presence of acids are examples of catalytic actions. Hydrogen peroxide can also be decomposed by a colloidal solution of platinum, which may be prepared as follows (Bredig): Two thick platinum wires dip into ice-cold water, and a current of about 10 amperes and 40 volts is employed. When the ends of the wires are kept 1-2 mm. apart, an electric arc passes between them, particles of platinum are torn off and remain suspended in the water. The solution is allowed to stand for some time, and filtered through a close filter. It represents a dark-coloured solution in which the particles cannot be detected with the ordinary microscope. A very dilute solution may be used to decompose hydrogen peroxide, and the reaction may be measured as described above when blood is employed.

Catalytic Action of Water—This may be illustrated by its effect on the combustion of carbon monoxide in air, which does not take place in the entire absence of water vapour. Carbon monoxide is prepared by the action of strong sulphuric acid on sodium formate and is carefully dried by passing through two wash-bottles containing strong sulphuric acid, and finally through a U tube containing phosphorus pentoxide. Some time before the experiment is to be tried, a little strong sulphuric acid is put in the bottom of a wide-mouthed bottle

with a close-fitting glass stopper, and the bottle allowed to stand, tightly stoppered, for some time.

The carbon monoxide issuing from the apparatus burns readily in air, but is immediately extinguished if the wide-mouthed bottle is placed over it. If, however, a small drop of water is placed in the tube whence the gas is issuing, the gas will continue to burn when the bottle is placed over it.

CHAPTER X

ELECTRICAL CONDUCTIVITY

Electrical Conductivity. General—From very early times it was noticed that electricity can be conveyed in two ways: (1) In conductors of the first class, more particularly metals, without transfer of matter; (2) in conductors of the second class—salt solutions or fused salts—with simultaneous decomposition of the conductor. We are here concerned only with conductors of the second class, but the use of the terms employed in electrochemistry may be illustrated by reference to conduction in metals.

For conductivity in general, Ohm's law holds, which may be enunciated as follows: *The strength of the electric current passing through a conductor is proportional to the difference of potential between the two ends of the conductor, and inversely proportional to the resistance of the latter.* Strength of current is usually represented by C, difference of potential or electromotive force by E, and resistance by R; Ohm's law may therefore be written symbolically as follows:—

$$C = \frac{E}{R}.$$

The practical unit of electrical resistance is the *ohm*, that of electromotive force the *volt*, and that of current the *ampere.* The strength of an electric current can be measured in various ways, perhaps most conveniently by finding the weight of silver liberated from a solution of silver nitrate in a definite interval of time. An ampere is that strength of current which in one second will deposit 0·001118 gram of silver from a solution of silver nitrate under certain definite conditions. Quantity of electricity is current strength × time; the amount of electricity

which passes in one second with a current strength of 1 ampere is a *coulomb*. When there is a difference of potential of 1 volt between two ends of a conductor, and a current of 1 ampere is passing through it, the resistance of the conductor is 1 ohm.

The resistance of a metallic conductor is proportional to its length and inversely proportional to its cross-section. Hence if l is the length and s the cross-section, the resistance R is given by $R = \rho\frac{l}{s}$, where ρ is a constant depending only on the material of the conductor, the temperature, etc., and is termed the *specific resistance*. If both l and s are equal to unity (1 cm.) the resistance is equal to ρ. The specific resistance, ρ, of a conductor is therefore the resistance in ohms which a cm. cube of it offers to the passage of electricity. If there is a difference of potential of 1 volt between two sides of the cube, and the current which passes is 1 ampere, the specific resistance of the cube is, by Ohm's law, = 1. A conductor of low resistance is said to have a high electrical conductivity, that is, it readily allows electricity to pass. Conductivity is therefore the converse of resistance, and *specific conductivity*, $\kappa = 1/\rho$, where ρ is specific resistance. Specific conductivity is measured in reciprocal ohms, sometimes termed mhos. In order to illustrate the magnitude of these factors, the specific resistance and the specific conductivity of a few typical substances at 18° are given in the table :—

Substance.	Silver.	Copper.	Mercury.	Gas carbon.	30 per cent. sulphuric acid.
Sp. resistance, ρ	0·0000016	0·0000017	0·00009	0·0050	0·74
Sp. conductivity, κ	624,000	587,000	10,240	200	1·35

Silver has the highest conductivity of all known substances; gas carbon is a comparatively poor conductor; and 30 per cent. sulphuric acid, one of the best conducting solutions, is enormously inferior to the metals in this respect.

Electrolysis of Solutions. Faraday's Laws—We now consider the phenomena accompanying the conduction of electricity in aqueous solutions of salts. If, for example, two platinum plates, one connected to the positive, the other to the

negative pole of a battery, are dipped into a solution of sodium sulphate, it will be observed that hydrogen is immediately given off at the plate connected to the negative pole of the battery, and oxygen at the plate connected to the positive pole. Further, if a few drops of litmus have previously been added to the solution, it will be noticed that the solution round the positive plate or pole becomes red, indicating the production of acid, and that round the negative pole becomes blue, showing the formation of alkali. An ammeter placed in the circuit will show that a current is passing through the solution, so that the chemical changes in question accompany the passage of the current. Even if the poles are far apart, the gases are liberated, and the acid and alkali appear *immediately connection is made through the solution*, and if the current is continued, the acid and alkali accumulate round the respective poles without any apparent change in the main bulk of liquid between the poles. These phenomena can scarcely be accounted for otherwise than by supposing that *matter travels with the current*, and that part travels towards the positive pole and part towards the negative pole. To these travelling parts of the solution Faraday gave the name of *ions*.

It will be well to mention here the nomenclature used in this part of the subject. A solution or fused salt which conducts the electric current is termed an *electrolyte*. The plate in the solution connected to the positive pole of the battery is termed the *positive pole*, *positive electrode*, or *anode*, that connected to the negative pole of the battery the *negative pole*, *negative electrode* or *cathode*. The ions which move towards the anode are often termed *anions*, those travelling towards the cathode *cations*.

We will now consider the relationship between the amount of chemical action and the quantity of electricity passed through a solution. The amount of chemical action might be estimated by measuring the volume of gas liberated at one of the poles, or by the amount of metal deposited on an electrode. This question was investigated by Faraday, and as a result he established a law which bears his name, and which may be enunciated as follows: *For the same electrolyte, the amount of chemical action is proportional to the quantity of electricity which*

passes.[1] Further, Faraday measured the relative quantities of substances liberated from *different* solutions by the same quantity of electricity, and was thus led to the discovery of his so-called second law: *The quantities of substances liberated at the electrodes when the same quantity of electricity is passed through different solutions are proportional to their chemical equivalents.* The chemical equivalent of any element (or group of elements) is equal to the atomic weight (or sum of the atomic weights) divided by the valency. The second law, therefore, states that if the same quantity of electricity is passed through solutions of sodium sulphate, cuprous chloride, cupric sulphate, silver nitrate, and auric chloride, the relative amounts of hydrogen and the metals liberated are as follows :—

Electrolyte	Na_2SO_4	$CuCl$	$CuSO_4$	$AgNO_3$	$AuCl_3$
Electrochem. equivalent	$H = 1{\cdot}008$; $O = \frac{16}{2}$;	$Cu = \frac{63{\cdot}4}{1}$;	$Cu = \frac{63{\cdot}4}{2}$;	$Ag = \frac{108}{1}$;	$Au = \frac{19}{3}$

The above result may also be expressed rather differently as follows: *The electrochemical equivalents* (the proportions of different elements set free by the same current) *are proportional to the chemical equivalents.*

That quantity of electricity which passes through an electrolyte when the chemical equivalent of an element (or group of elements) in grams is being liberated will obviously be a quantity of very considerable importance in electrochemistry. Since 1 ampere in 1 second (a coulomb) liberates 0·001118 gram of silver, it follows that when the chemical equivalent of silver or any other element is liberated, $107{\cdot}88/0{\cdot}001118 = 96500$ coulombs must pass through the electrolyte. It is often designated by the symbol F (faraday). One coulomb will therefore liberate $35{\cdot}46/96500 = 0{\cdot}000368$ gram of chlorine, $127/96500 = 0{\cdot}001316$ gram of iodine, and $1{\cdot}008/96500 = 0{\cdot}000010445$ gram of hydrogen.

Mechanism of Electrical Conductivity—It has already been pointed out (p. 243) that during the electrolysis of sodium sulphate the products of electrolysis appear only at the poles,

[1] Faraday measured the amount of electricity by its action on a magnetic needle.

the main bulk of solution between the poles begin apparently unaffected. This is most readily accounted for on the view that part of the solute is moving towards the positive and part towards the negative pole, these moving parts being termed anions and cations respectively. We now assume further that the cations are charged with positive electricity, and move towards the negatively charged cathode owing to electrical attraction; similarly, the negatively charged anions are attracted to the anode. When the ions reach the poles, they give up their charges, which neutralize a corresponding amount of the opposite kinds of electricity on the anode and cathode respectively, and then appear as the elements or compounds we are familiar with. The process of electrolysis is illustrated in Fig. 32. Into the vessel containing sodium sulphate solution dip two electrodes (on opposite sides of the vessel) connected with the positive and negative poles of the battery respectively. The direction of motion of the ions to the oppositely-charged poles is illustrated by the arrows.

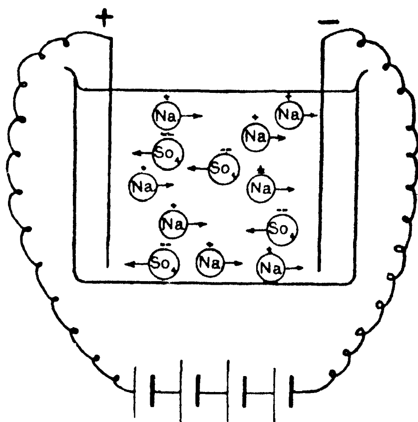


Fig. 32.

It should be pointed out that there can be no appreciable separation of ions in the solution in the sense that positive ions accumulate towards one side and negative ions towards the other. The reason is that even a very slight separation sets up large electric fields of force which oppose further separation. The ions are free, and tend to move in opposite directions, but owing to the electric forces the whole salt drifts in the direction of the faster moving ion.

It is not always an easy matter to say what the moving ions are. It is only rarely that they are set free as such, since

secondary reactions often take place at the electrodes. When a strong solution of cupric chloride is electrolysed, copper and chlorine are liberated at the cathode and anode respectively, and it is probable that these substances are the ions. In the case of sodium sulphate, however, for which hydrogen and oxygen are the products of electrolysis, secondary reactions must take place. The current is in all probability conveyed through the solution by Na and SO_4 ions. When the former reach the cathode, they give up their charges and form metallic sodium, which immediately reacts with the water, forming sodium hydroxide and hydrogen. In the same way the SO_4 ions, on reaching the anode, give up their charges, and the free SO_4 group then reacts with the water according to the equation $SO_4 + H_2O = H_2SO_4 + O$, oxygen being liberated and sulphuric acid regenerated. In this way the phenomena already described are readily accounted for.

So far, we have assumed that the material of the electrodes is not acted on by the products of electrolysis. This is generally true when the electrodes are made of platinum or other resistant metal, but in other cases secondary reactions take place between the discharged ions and the poles. Thus when a solution of copper sulphate is electrolysed between copper poles, the SO_4 ions, after losing their charges, react with the anode according to the equation $Cu + SO_4 = CuSO_4$, so that the net result of the electrolysis of copper sulphate between copper poles is the transfer of copper from the anode to the cathode.

We have assumed that in a solution of sodium sulphate the moving ions are Na and SO_4. As the Na ion moves towards the negative electrode, it must already be positively charged; this may be indicated thus: $\overset{+}{Na}$ (Fig. 32), or, more concisely, by a dot, thus: $Na^{\cdot}$. As neither positive nor negative electricity accumulates in the solution during electrolysis, the amount of positive electricity neutralized on the anode must be equivalent to that neutralized on the cathode. Hence, since two sodium ions are discharged for every SO_4 ion, the latter must carry double the amount of electricity that a sodium ion carries, and this is indicated by the symbols $\overset{=}{SO_4}$ or SO_4'' (Fig. 32).

According to our present views, the metallic components of salts in solution are positively charged, the number of charges corresponding with the ordinary valencies of the metals. Some important cations are $K^{\cdot}$, $Na^{\cdot}$, $Ag^{\cdot}$, $NH_4^{\cdot}$, $Ca^{\cdot\cdot}$, $Hg_2^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, etc. The remainder of the salt molecule constitutes the negative ion, which, like the positive ion, may have one, two or more (negative) electric charges. Among the more important anions are Cl', Br', I', NO_3', SO_4'', CO_3'', PO_4''', etc. Acids and bases deserve special consideration from this point of view. Since salts are derived from acids by replacing the hydrogen by metals, it is natural to suppose that the positive ion in aqueous solutions of acids is $H^{\cdot}$, and that the remainder of the molecule constitutes the negative ion. On the other hand, aqueous solutions of all bases contain the OH' group. These points are dealt with fully at a later stage.

Freedom of the Ions before Electrolysis—The fact that the ions begin to move towards the respective electrodes immediately the current is made appears to indicate that they are electrically charged in the solution before electrolysis is commenced. The questions therefore arise as to the state of such a salt as sodium chloride in dilute solution, and as to what occurs when the circuit is completed. The view long held was that the atoms are united to form a molecule, NaCl, at least partly owing to the electrical attraction of their contrary charges, and that the current pulls them apart during electrolysis. Careful measurements show, however, that Ohm's law holds for electrolytes, from which it follows that *the electrical energy expended in electrolysis is entirely used up in overcoming the resistance of the electrolyte, so that no work is done in pulling apart the components of the molecule.* On the basis of this observation, and in agreement with certain views previously enunciated by Williamson as to the kinetic nature of equilibrium in general (*cf.* p. 167), Clausius showed that the equilibrium condition in electrolytes cannot be such that the ions of contrary charge are firmly bound together; on the contrary, the equilibrium must be of a kinetic nature, so that the ions are continuously exchanging partners, and must, *at least momentarily*, be present in solution as free ions. The average fraction of the ions free under definite conditions of temperature and dilution was not estimated by Clausius, but he

considered that the fraction was probably very small. Clausius's theory accounts for the qualitative phenomena of electrolysis, as during their free intervals the ions would be progressing towards the oppositely charged poles, and would finally reach them and be discharged.

The views of Clausius were further developed in 1887 by Arrhenius,[1] who first showed how the fraction of the molecules split up into ions could be deduced from electrical conductivity measurements, and independently from osmotic pressure measurements. This constitutes the main feature of the theory of electrolytic dissociation, which is dealt with in detail later (p. 266), and the fact that the two methods for determining the fraction of the molecules present as free ions gave results in very satisfactory agreement contributed much to the general acceptance of the theory. In a normal solution of sodium chloride, then, there is an equilibrium between free ions and non-ionized molecules, represented by the equation $NaCl \rightleftarrows Na^{\cdot} + Cl'$, in which, according to Arrhenius, about 70 per cent. of the salt is ionized and the remaining 30 per cent. is present as NaCl molecules. *According to this theory, the electrical conductivity is determined exclusively by the free ions, and not at all by the non-ionized molecules or by the solvent.*

Dependence of the Conductivity on the Number and Nature of the Ions—We are now in a position to form a picture of the mechanism of electrical conductivity in a solution. Suppose there are two parallel electrodes 1 cm. apart (Fig. 32) with the electrolyte between them, and that the difference of potential between the electrodes is kept constant, say at 1 volt. Before the electrodes are connected with the battery, the ions are moving about in all directions through the solution. When connection is made—in other words, when the electrodes are charged—they exert a *directive force* on the charged ions, which move towards the poles with the contrary charges. Those nearest the poles arrive first, give up their charges to the poles, thus neutralizing an equivalent amount of electricity on the latter, and then either appear in the ordinary uncharged form (*e.g.*, copper), react with the solvent (*e.g.*, SO_4 when platinum electrodes are used), with the electrodes (*e.g.*, SO_4 with copper

[1] *Zeitsch. physikal. Chem.*, 1887, **1**, 631.

electrodes), or with each other. It will be seen that the process does not consist in the *direct* neutralization of the electricity on the positive electrode by that on the negative electrode, but part of the charge on the anode is neutralized by the anions, whilst an equivalent amount of charge on the cathode is neutralized by the cations—a process which has the same ultimate effect as direct neutralization.

On this basis it is clear that with a constant E.M.F. the rate at which the charges on our two plates are neutralized, in other words, the conductivity of the solution between them, depends on three things: (1) the number of carriers or ions per unit volume; (2) the load or charge which they carry; (3) the rate at which they move to the electrodes. Each of these factors will now be briefly considered.

(1) *The Number of Ions*—Other things being equal, the conductivity of a solution will clearly be proportional to the number of ions per unit volume. For the same electrolyte, the number of ions can, of course, be varied by varying the concentration of the solution. In general, it may be said that on increasing of concentration the ionic concentration also increases, but the exact relationship will be dealt with later. For different electrolytes of the same equivalent concentration, the conductivity will depend on the extent to which the solute is split up into its ions and on their speed.

(2) *The Charge Carried by the Ions*—As has already been pointed out, there is a simple relationship between the capacity of different ions for transporting electricity, since the gram-equivalent of any ion (positive or negative) conveys 96,500 coulombs. Thus if in an hour (= 3600 seconds) a gram-equivalent of sodium (23 grams) and of chlorine (35·46 grams) are discharged at the respective electrodes, the current which has passed through the cell is

$$\frac{96,500}{3600} = 26{\cdot}8 \text{ amperes.}$$

(3) **Migration Velocity of the Ions**—In this section we will for simplicity consider only univalent ions, but the same considerations apply to all electrolytes. Since positive and negative ions are necessarily discharged in equivalent amount (p. 246),

and the number of positive and negative univalent ions discharged in a given time is therefore equal, it might be supposed that the ions must travel at the same rate. This, however, is by no means the case. Our knowledge of this subject is mainly due to Hittorf, who showed that the *relative speeds of the ions could be deduced from the changes in concentration round the electrodes after electrolysis.*

The effect of the unequal speeds of the ions on the concentrations round the poles is made clear by the accompanying scheme (Fig. 33), a modified form of one given by Ostwald.

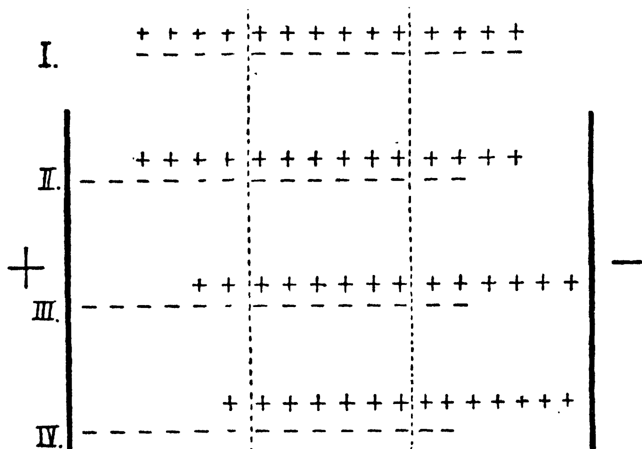


Fig. 33.

The vertical dark lines represent the anode and cathode respectively, and the dotted lines divide the cell into three sections, those in contact with the electrodes being termed the anode and cathode compartments respectively. The positive ions are represented by the usual + sign, and the negative ions by the — sign. I. represents the state of affairs in the solution before connection is made; the number of anions is the same as that of the cations, and the concentration is uniform throughout. The remaining lines represent the state of affairs in the solution after electrolysis on different assumptions as to the relative speeds of the ions. Suppose at first that only the negative

ions move. The condition of affairs in the solution when all the negative ions have moved two steps to the left is shown in II. Each ion left without a partner is supposed to be discharged, and the figure shows that although the positive ions have not moved an equal number of positive ions is discharged. Further, whilst the concentration in the anode compartment has not altered during the electrolysis, the concentration in the cathode compartment has been reduced by half.

Suppose now that the positive and negative ions move at the same rate. The state of affairs when each ion, positive or negative, has moved two steps towards the oppositely-charged pole is represented in III. It is evident that four positive and four negative ions have been discharged, and that the concentration of undecomposed salt has diminished in both compartments, and to the same extent, namely by two molecules.

Finally, let us assume that both ions move, but at unequal rates, so that the positive ions move faster than the negative ions in the ratio 3 : 2. The state of affairs when the positive ions have moved three steps to the right, and the negative ions two steps to the left, is shown in IV. It is clear that five positive and five negative ions have been discharged, and that whilst there is a fall of concentration of two molecules round the cathode, there is a fall of three round the anode.

These results show that the fall of concentration round any one of the electrodes is proportional to the speed of the ion *leaving* it. In II., for example, there is a fall of concentration round the cathode, but not round the anode, corresponding with the fact that the anion moves, but not the cation. Similarly, in III., the fall of concentration round anode and cathode is equal, corresponding with the fact that the anion and cation move at the same. Finally, in IV., fall round anode : fall round cathode : : 3 : 2, corresponding with the fact that speed of cation : speed of anion = 3 : 2. From these examples we obtain the important rule that

$$\frac{\text{Fall of concentration round anode}}{\text{Fall of concentration round cathode}} = \frac{\text{speed of cation}}{\text{speed of anion}}.$$

The student often finds a difficulty in understanding how, as in IV., five ions can be discharged at the anode when only two

anions have crossed the partitions. To account for this, it must be assumed that there is always an excess of ions in contact with the electrodes, so that more are discharged than actually arrive by diffusion.

The speed of the cations is often represented by u, and that of the anions by v. The total quantity of electricity (say, unit quantity) carried is proportional to $(u + v)$, and, of this total $n = v/(u + v)$ is carried by the anions and $1 - n = u/(u + v)$ by the cations. n, the fraction of the current carried by the anion, is termed the *transport number* of the anion; similarly, $1 - n$ is the transport number of the cation.

It is evident from the figure that there is a central section of the cell between the dotted lines in which no change of concentration takes place when electrolysis is not carried too far. Therefore, in order to investigate the changes in concentration, it is simply necessary to remove the solutions round the electrodes after electrolysis and analyse them, but *the experiment will only be successful if the intermediate layer has not altered in strength.*

Practical Determination of the Relative Migration Velocities of the Ions—The experiment may conveniently be made in the modified form of Hittorf's apparatus used in Ostwald's laboratory (Fig. 34). It consists of two glass tubes communicating towards the upper ends; one of them is closed at the lower end, and the other provided with a stopcock, as shown. The electrodes, A and K, are sealed into glass tubes which pass up through the liquid, and communication with a battery is made in the usual way by means of wires which pass down the interior of the glass tubes.

As an illustration, the determination of the transport numbers of the Ag' and NO_3' ions in a solution of silver nitrate will be described. The anode A is of silver, and should be covered with finely-divided silver by electrolysis just before the experiment; the cathode is of copper. The electrodes are placed in position, the anode compartment filled up to the connecting tube with 1/20 normal silver nitrate, the cathode compartment up to B with a concentrated solution of copper nitrate, and finally the apparatus is carefully filled up with the silver nitrate solution in such a way that the boundary between the two solutions at B remains fairly sharp. The cell is then connected *in series* with a high adjust-

able resistance, an ammeter, and a silver voltameter, and then joined to the terminals of a continuous current lighting curcuit (110 volts) in such a way that the silver pole becomes the anode. By means of the variable resistance, the current is so adjusted that a current of about 0·01 ampere is obtained (to be read off on the ammeter), and the electrolysis continued for about two hours. Finally, a measured amount (about 3/4) of the anode solution is run off and titrated with thiocyanate in the usual way. The strength of the current can be read off on the ammeter, and from this and the time during which the current has passed, the total quantity of electricity passed through the solution can be calculated. It is, however, preferable to employ for this purpose the silver voltameter above referred to. It consists of a tube with stopcock similar to the left-hand part of the transport apparatus (Fig. 34), and is provided with a silver electrode (to serve as anode) similar to that in the other apparatus, and placed in a corresponding position (in the lower part of the tube). The tube is filled to 3/4 of its length with a 15-20 per cent. solution of sodium or potassium nitrate, and carefully filled up with dilute nitric acid so that the two solutions do not mix. The cathode, of platinum foil, dips in the nitric acid. During electrolysis, the NO_3' ions dissolve silver from the anode, and by titrating the whole of the contents with ammonium thiocyanate after the experiment, the amount of silver in solution can be determined, and from this the quantity of electricity which has passed through the solution can readily be calculated (p. 244).

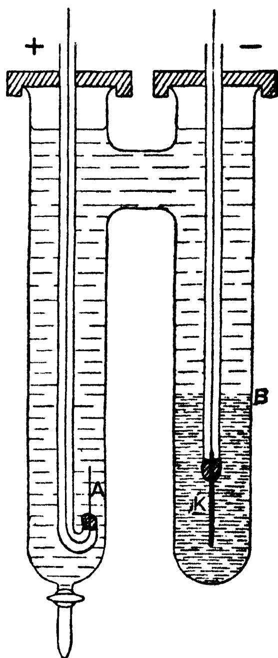


FIG. 34.

We now return to the transport apparatus. For our purpose

it will be sufficient to deal only with the change of concentration in the anode compartment. From this the transport number of the cation is obtained, and the transport number of the anion is then at once obtained by difference. During electrolysis, the silver concentration round the anode *diminishes* owing to migration of silver ions towards the cathode. The process may conveniently be illustrated by III. of Fig. 33 where the fall owing to migration is from 4 to 2. At the same time, however, NO_3 ions reach the anode, and after being discharged dissolve silver from it, the silver concentration in the anode compartment therefore *increasing*. The latter effect is the same as that taking place simultaneously in the silver voltameter, as described above, and therefore, *if no silver migrated from the anode*, the total increase of concentration in this compartment would be equal to that in the silver voltameter, which, as explained above, is a measure of the total quantity of electricity which passes; we will term this a. If b is the (unknown) change in concentration due to the migration of the silver ions, the *observed* change in concentration at the anode will be $a - b$. As a is known, and $a - b$ is found by titrating the anode solution after the experiment, b can readily be obtained.

In practice, the greater part of the anode solution after electrolysis is run into a beaker, it is then weighed or an aliquot part measured, and titrated.

The calculation of the results will be rendered clear from the details of an experiment made in Ostwald's laboratory. Before the experiment 12·31 grams of the silver nitrate solution required 26·56 c.c. of a 1/50 n potassium thiocyanate solution, so that 1 gram of solution contained 0·00739 gram of silver nitrate. After the experiment, 23·38 grams of the anode solution required 69·47 c.c. of the thiocyanate solution, corresponding to 0·2361 gram of silver nitrate. The solution, therefore, contained 23·14 grams of water, which before the experiment contained $23·14 \times 0·00739 = 0·1710$ gram of silver nitrate, hence the increase of concentration at the anode is 0·0651 gram $= a - b$. The contents of the silver voltameter required 36·16 c.c. of thiocyanate $= 0·1229$ gram of silver nitrate $= a$; the same amount is dissolved at the anode

in the transport apparatus. As the actual increase of concentration was only 0·0651 gram, 0·1229 − 0·0651 = 0·0578 gram of silver must have left the anode compartment by migration. Hence the transport number for silver is

$$1 - n = \frac{u}{u + v} = \frac{0{\cdot}0578}{0{\cdot}1229} = 0{\cdot}470,$$

and for the NO_3' ion

$$n = \frac{v}{u + v} = \frac{0{\cdot}0651}{0{\cdot}1229} = 0{\cdot}530.$$

Hence, of the total current, 47 per cent. is carried by the silver ions, and 53 per cent. by the NO_3' ions.

It was shown by Hittorf that the transport numbers are practically independent of the E.M.F. between the electrodes, but depend to some extent on the concentration and on the temperature. It is remarkable that at higher temperatures they tend to become equal. Some of the numbers are given in the next section.

Specific, Molecular, and Equivalent Conductivity—Just as in the case of metallic conduction, the resistance of an electrolyte is proportional to the length, and inversely proportional to the cross-section of the column between the electrodes. Hence we may define the specific resistance of an electrolyte as the resistance in ohms of a cm. cube, and its specific conductivity as 1/specific resistance, expressed in reciprocal ohms. Since, however, the conductivity does not depend on the solvent but on the solute, it is much more convenient to deal with solutions containing quantities of solute proportional to the respective molecular weights. The so-called *molecular conductivity*, μ, is most largely used in this connection; it is the conductivity, in reciprocal ohms, of a solution containing 1 mol of the solute when placed between electrodes exactly 1 cm. apart. It may also be defined as the specific conductivity, κ, of a solution, multiplied by v, the volume in c.c. which contain a mol of the solute. Hence we have

$$\mu = \kappa v.$$

As an example, the following values for the specific and molecular conductivities of solutions of sodium chloride at 18°, as given by Kohlrausch, may be quoted:—

Concentration of Solution.	Sp. Conductivity, κ.	Molecul Conductiv κv.
1·0 molar (v = 1,000)	0·0744	74·4
0·1 molar (v = 10,000)	0·00920	92·0
0·01 molar (v = 100,000)	0·001020	102·0
0·001 molar (v = 1,000,000)	0·0001065	106·5
0·0001 molar (v = 10,000,000)	0·00001081	108·1

It will be noticed that the molecular conductivity as defined above increases at first with dilution, but beyond a certain point remains practically constant on further dilution.

These numbers enable us to illustrate more fully the physical meaning of the molecular conductivity. Imagine a cell of 1 cm. cross-section and of unlimited height, two opposite walls throughout the whole height acting as electrodes. If a litre of a molar solution of sodium chloride is placed in the cell, it will stand at a height of 1000 cms. We may regard the solution as made up of cm. cubes, 1000 in number, and if the conductivity of one of these cubes—the specific conductivity—is κ_1, the total conductivity (in other words the molecular conductivity) is $1000\kappa_1$. If now another litre of water is added, the height of the solution will be 2000 cms. and its molecular conductivity is now $2000\kappa_2$, where κ_2 is the specific conductivity of the half-molar solution. In exactly the same way, the molecular conductivity may be determined at still greater dilutions. From the above it is clear that a measure of the conducting power of a mol of the electrolyte in different dilutions is obtained by multiplying the volume in c.cs. in which the electrolyte is dissolved by its specific conductivity at that dilution, or in symbols

$$\mu = \kappa v$$

as given above.

A glance at the last two lines in the table helps us to understand the approximately constant value of μ in very dilute solutions. When the solution is diluted from 1/1000 to

1/10,000 molar, the specific conductivity is reduced to about 1/10, but as the volume is ten times as great, the molecular conductivity is only slightly altered.

Besides the molecular conductivity, the term *equivalent conductivity*, λ, is sometimes used. As the name implies, it is the specific conductivity of a solution multiplied by the volume in c.c. which contains a *gram-equivalent* of the solute.

Kohlrausch's Law. Ionic Velocities—The numbers in the third column of the above table show that the molecular conductivity of sodium chloride increases, at first rapidly and then very slowly, with dilution. This subject was investigated for a number of solutions by Kohlrausch, who found that for solutions of electrolytes of high conductivity (salts, so-called "strong" acids and bases) the molecular conductivity increases with dilution up to about 1/10000 molar solution, and beyond that point remains practically constant on further dilution. Kohlrausch showed further that this limiting value of the molecular conductivity, which may be represented by μ_∞, is different for different salts, and may be regarded as the sum of two independent factors—one pertaining to the cation or positive part of the molecule, the other to the anion, or negative part of the molecule. This experimental result is termed Kohlrausch's law, and is readily intelligible on the basis of the theory of electrical conductivity developed above. The limiting value of the molecular conductivity is reached when the molecule is completely split up into its ions; under these circumstances *the whole of the salt takes part in conveying the current.* For simplicity we will consider solutions of binary electrolytes. In very dilute equimolar solutions of different electrolytes, the number of the ions and their charges are the same, and the observed differences of μ_∞ can only be due to the different speeds of the ions. The limiting molecular conductivities of binary electrolytes are therefore proportional to the sum of the speeds of the ions, and when the units are properly chosen we have

$$\mu_\infty = u + v,$$

where u is the speed of the cation, v that of the anion. This is the mathematical form of Kohlrausch's law, and expresses the

very important result that in sufficiently dilute solution the speed *of an ion is independent of the other ion present in solution.*

From the results of conductivity measurements, only the sum of the speeds of the ions can be deduced, but, as has already been shown, the relative values of u and v can be obtained from the results of migration experiments (p. 252). It was found by Kohlrausch that the value of $\mu_\infty = u + v$ for silver nitrate at 18° is 116·0. The accurate value for the transport number of the anion, NO_3', is $n = v/(u + v) = 0{\cdot}530$. Hence $v = 0{\cdot}530 \times 116{\cdot}0 = 61{\cdot}7$ and $u = 0{\cdot}470 \times 116{\cdot}0 = 54{\cdot}3$. The values of u and v, expressed in these units, are termed the *ionic velocities*, under the conditions of the experiment. The accompanying table gives the ionic velocities, calculated from the results of conductivity and transport measurements, for some of the more common ions in infinite dilution[1] at 18°, expressed in the same units as the molecular conductivity of sodium chloride (p. 256):—

H· = 318	Li· = 33	OH′ = 174
K· = 65	NH_4· = 64	Cl′ = 66
Na· = 44	Ag· = 54	I′ = 67
		NO_3' = 62

It is interesting to observe that the velocity of the H· ion is relatively very high, about five times as great as that of any of the metallic ions. The ion which comes next to it is the OH′ ion, the speed of which is more than half that of the H· ion, and much greater than that of any of the other ions. Since the conductivity of a solution is, as we have already seen, proportional to the speed of the ions, it follows that the solutions of highly ionized acids and bases will have a relatively high conductivity. Thus, under conditions otherwise equal as regards concentration, ionization, temperature, etc., the conductivities of dilute solutions of hydrochloric acid and of sodium chloride will be in the ratio (318 + 66) = 381 to (44 + 66) = 110, or about 3·5 : 1.

Absolute Velocity of the Ions. Internal Friction—The absolute velocity of the ions is proportional to the E.M.F. between

[1] The more concentrated the solution, the smaller are the ionic velocities, owing to the increased resistance to their motion.

the electrodes, and inversely proportional to the resistance offered to their passage by the solvent. When the fall of potential is 1 volt per c.m. (*i.e.*, when the difference of potential between the electrodes is x volts and the distance between them is x cm.) it can be shown that the absolute velocities, in cm. per second, are obtainable from the values for the ionic velocities given above by dividing by 96,500 or, what is the same thing, by multiplying by $1 \cdot 036 \times 10^{-5}$.

Consider the transport of electric current through a cm. cube of electrolyte. As already pointed out, the strength of the current depends upon the number of ions, on their speed and on the charge which they carry. If c is the concentration of the electrolyte in gram-equivalents per c.c., α is the degree of dissociation and U_1 and V_1 the speed of the cation and anion respectively, in cm. per second, the current passing through the cm. cube is $96{,}500\,\alpha c\,(U_1 + V_1)$ amperes, 96,500 coulombs being the charge carried by 1 gram-equivalent of electrolyte. The current may also be represented as the product of the specific conductivity, κ, and the difference of potential, E, between the two sides of the cube. Therefore

$$E\kappa = 96{,}500\,\alpha c\,(U_1 + V_1).$$

Now κ/c or κv is the equivalent conductivity of the solution, which we will term λ. If, further, the potential gradient is 1 volt per cm. $E = 1$ and the above equation simplifies to

$$\lambda = 96{,}500\,\alpha\,(U + V)$$

where U and V represent the speed of the ions, in cm. per second, when the potential gradient is 1 volt per cm.

When dissociation is complete $\alpha = 1$ and the above formula, in the case of a binary uni-univalent electrolyte, for which $\lambda_\infty = \mu_\infty$ becomes (*cf.* p. 257)

$$\mu_\infty = u + v = 96{,}500\,(U + V).$$

From this equation it follows that the speed of the ions in cm. per second are obtainable from the velocities expressed in the ordinary units by dividing by 96,500.

Hence the absolute velocity of the hydrogen ion is, under the

conditions described, $318 \times 1{\cdot}036 \times 10^{-5} = 0{\cdot}00332$ cm. per second, and of the potassium ion 0·00067 cm. per second at infinite dilution. The speed of the ions is therefore extremely low; even the hydrogen ions, under a driving force of 1 volt per cm., only move about twice as fast as the extremity of the minute hand of an ordinary watch. This very slow motion of the moving particles indicates that the resistance to their passage through the solvent is very great. Kohlrausch has calculated that the force required to drive a gram of sodium ions through a solution at the rate of 1 cm. per second is 153×10^6 kilograms weight, or about 150,000 tons weight.

The absolute velocity of the ions can also be measured directly by a method the principle of which is due to Lodge, and which may be illustrated by an experiment described by Danneel. A U-tube is partly filled with dilute nitric acid and in the lowest part of the tube a solution of potassium permanganate, the specific gravity of which has been increased as much as possible by the addition of urea, is carefully placed, by means of a pipette, in such a way that the boundary between the acid and the permanganate remains sharp. When platinum electrodes are dipped in the nitric acid in the two limbs, and a current passed through the solution, the violet boundary (due to the coloured MnO_4' ion) moves towards the anode. From the observed speed of the boundary and the difference of potential between the poles, the speed of the ion for a fall of potential of 1 volt/cm. is obtained, and has been found to agree exactly with the value obtained by conductivity and transport measurements.

This method is not confined to salts with coloured ions, but the moving boundary can also be observed with colourless solutions when, as is usually the case, the refractive index of the two solutions is different. There are, of course, two boundaries, one due to the positive ions moving towards the cathode, and the other due to the negative ions moving towards the anode. When the conditions are such that both can be observed, the relative speeds give the ratio u/v directly.

Measurements of ionic velocities on this principle have been made by Masson, Steele and others, and the results are in entire agreement with those obtained indirectly.

Experimental Determination of Conductivity of Electrolytes—The measurement of the conductivity of conductors of the first class is a very simple operation. Until comparatively recently, however, no very satisfactory results for the conductivity of electrolytes could be obtained, because when a steady current is passed through a solution between platinum electrodes the products of electrolysis accumulate at the poles and set up a back E.M.F. of uncertain value, a phenomenon known as polarization (p. 396). This difficulty is, however, completely got over by using an alternating instead of a direct current (Kohlrausch, 1880); by the rapid reversal of the current the two electrodes are kept in exactly the same condition, and there is no polarization.

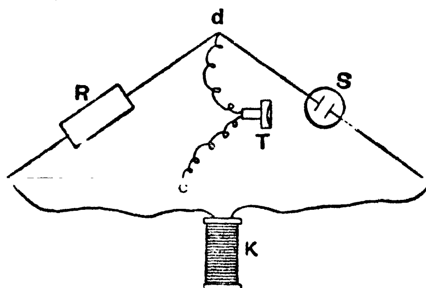


FIG. 35.

The arrangement of the apparatus, which in principle amounts to the measurement of resistance by the Wheatstone bridge method, is shown in Fig. 35. R is a resistance box, S a cell with platinum electrodes, between which is the solution the resistance of which is to be measured, *ab* is a platinum wire of uniform thickness, which may conveniently be a metre long, and is stretched along a board graduated in millimetres, *c* is a sliding contact. By means of a battery (not shown in the figure) a direct current is sent through a Ruhmkorff coil, K, the latter then gives rise to an alternating current, which divides at *a* into two branches, reaching *b* by the paths *adb* and *acb* respectively. As a galvanometer is not affected by an alternating current, it is in this case replaced by a telephone T, which is silent when the points *c* and *d* are at the same potential.

The contact-maker, *c*, is shifted along the wire till the telephone no longer sounds. Under these circumstances, the following relationship holds—

$$\frac{\text{Length of } ac}{R} = \frac{\text{Length of } cb}{S},$$

and since *ac*, *cb* and R are known, S, the resistance of the part of the electrolyte between the electrodes, can at once be calculated.

As the resistance of electrolytes varies within wide limits, different forms of cell are employed according to circumstances.

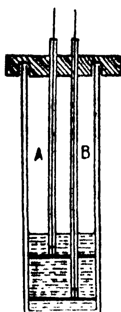


FIG. 36.

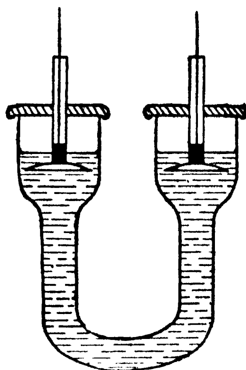


FIG. 37.

For solutions of small conductivity, the Arrhenius form represented in Fig. 36 is very suitable. The electrodes, which are stout platinum discs 2-4 cm. in diameter, are fixed (by welding or otherwise) to platinum wires, which are sealed into glass tubes A and B, as shown in the figure. These glass tubes are fixed firmly into the ebonite cover of the cell, so that the distance between the electrodes remains constant, and electrical connection is made in the usual way by wires passing down the interior of the glass tubes. In order to expose a larger surface, and thus minimize polarization effects, which would interfere with the sharpness of the minimum in the telephone, the electrodes are coated with finely-divided platinum by electrolysis of a solution of chlorplatinic acid. For electrolytes of high

conductivity, a modified form of conductivity vessel, with smaller electrodes placed further apart, has been found convenient (Fig. 37).

Experimental Determination of Molecular Conductivity—It is clear that the observed resistance of the electrolyte must depend on what is usually termed the *capacity* of the cell, that is, on the cross-section of the electrodes and the distance between them. The specific conductivity, and hence the specific resistance, of the electrolyte could be calculated if these two magnitudes were known (p. 242); but it is much simpler to determine the "constant" of the vessel, which is proportional to its capacity, by using an electrolyte of known conductivity. For this purpose, a 1/50 molar solution of potassium chloride may conveniently be used for cells of the first type. The method of procedure will be clear from an example. Referring to the figure, we have, for the resistance, S, of the electrolytic cell

$$S = \frac{R \cdot bc}{ac} \text{ and conductivity } C = \frac{1}{S} = \frac{ac}{R \cdot bc}.$$

Further, since the specific conductivity, κ, must be proportional to the observed conductivity, we have

$$\kappa = AC = A\frac{ac}{R \cdot bc},$$

where A is a constant. Since all the other factors, including κ, the specific conductivity of potassium chloride, are known, A, the constant of the cell, can be calculated. If, now, with the same distance between the electrodes, a solution of unknown specific conductivity, κ_1, is put in the cell, and for the resistance R' the new position of the contact is c', the specific conductivity in question is given by the formula

$$\kappa_1 = A\frac{ac'}{R' \cdot bc'}.$$

By multiplying κ_1 by the number of c.c. containing 1 mol of the solute, the molecular conductivity is obtained.

An alternative method of calculating κ_1 without reference to the cell constant is as follows. If S and S_1 represent the

resistances of the cell containing N/50KCl and the solution of specific conductivity κ_1 respectively, then

$$\kappa_1 = \frac{\kappa S}{S_1}.$$

From the results of conductivity measurements in different dilutions, μ_∞ can readily be obtained directly for salts, strong acids and basis; it is the value to which μ approximates on progressive dilution. μ_∞ cannot, however, be obtained directly for weak electrolytes, such as acetic acid and ammonia; before the limiting value of the conductivity is reached with these electrolytes, the solutions would be so dilute as to render accurate measurement of the specific conductivity impossible. This difficulty is got over by making use of Kohlrausch's law. The value of μ_∞ for acetic acid must be the sum of the velocities of the H· and CH_3COO' ions. The former is obtained from the results of conductivity and transport measurements with any strong acid, and has the value 318 at 18°. In a similar way the velocity of the CH_3COO' ion can be obtained from observations with an acetate for which the value of μ_∞ can conveniently be found, *e.g.* sodium acetate. μ_∞ for the latter salt at 18° is 78·5, and as the velocity of the Na· ion is 43·5 at infinite dilution, that of the CH_3COO' ion must be 78·5 − 43·5 = 35·0. Hence for acetic acid

$$\mu_\infty = u + v = 35{\cdot}0 + 318 = 353{\cdot}0 \text{ at } 18°.$$

Results of Conductivity Measurements—In general, it may be said that the conductivity of pure liquids is small. Thus the specific conductivity of fairly pure distilled water is about 10^{-6} reciprocal ohms at 18°, and even this small conductivity is largely due to traces of impurities. It is a remarkable fact that the specific conductivity of a number of other liquids, which have been purified very carefully by Walden,[1] is of the same order as that given above for water.

Mixtures of two liquids have in many cases a very small conductivity, not appreciably greater than that of the pure liquids themselves; this is true of mixtures of glycerine and

[1] *Zeitsch. Physikal. Chem.*, 1903, **46**, 103.

water, and of alcohol and water. On the other hand, a mixture of two liquids which are practically non-conductors may have a very high conductivity—for example, mixtures of sulphuric acid and water. The results obtained for this mixture are represented in Fig. 38, the acid concentration being measured along the horizontal axis, and the specific conductivity along the vertical axis. The figure shows that, on gradually adding sulphuric acid to water, the specific conductivity of the mixture increases till 30 per cent. of acid is present, reaches a maximum value at that point, and on further addition of acid diminishes. When pure sulphuric acid is present (100 per cent.

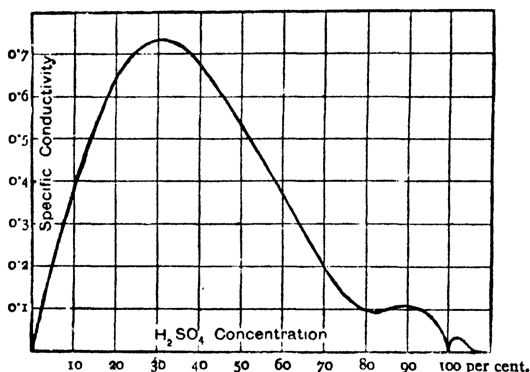


FIG. 38.

on curve), the conductivity is practically zero, and is increased both by the addition of water (left-hand part of curve) and of sulphur trioxide (right-hand part of curve). Further, the curve has a minimum between 84 and 85 per cent. of acid, which, it is interesting to note, exactly corresponds with the composition of the monohydrate H_2SO_4, H_2O. According to the electrolytic dissociation theory, the conductivity depends on the presence of free ions, and the curve for sulphuric acid and water shows in a very striking way that *the condition most favourable for ionization is the presence of two substances*. Why ions are formed in a mixture of sulphuric acid and water, and not appreciably, if at all, in a mixture of alcohol and water, is not well understood (*cf*. p. 340).

Analogous phenomena are met with for solutions of solids and of other liquids in liquids. An aqueous solution of sugar has no appreciable conducting power. The so-called "strong" acids and bases form well-conducting liquids with water. The conductivity of most organic acids and bases is small, and in corresponding dilution ammonium hydroxide is a much poorer conductor than potassium hydroxide. On the other hand, all salts, even the salts of organic acids which are themselves weak, have a very high conductivity.

The conductivity of substances in solvents other than water is usually small, but solutions in methyl and ethyl alcohols and in liquid ammonia are exceptions. The dependence of electrical conductivity on the nature of the solvent will be discussed later.

It is interesting to note that many fused salts, such as silver nitrate and lithium chloride, are good conductors, and thus form an exception to the rule that pure substances belonging to the second class of conductors have a very small conductivity.

Electrolytic Dissociation—It has already been pointed out (p. 134) that solutions of salts, strong acids and bases, have a much higher osmotic pressure in aqueous solution than would be the case if Avogadro's hypothesis was valid for these solutions. According to the molecular theory, the solutions behave as if there were more particles of solute present than would be anticipated from the simple molecular formula, and van't Hoff expressed this by a factor i, which represented the ratio between the observed and calculated osmotic pressures. This was the position of the theory of solution in 1885.

About that time, Arrhenius pointed out that there is a close connection between electrical conductivity and abnormally high osmotic pressures; *only those solutions which, according to van't Hoff's theory, have abnormally high osmotic pressures, conduct the electric current.* Kohlrausch had previously shown that the molecular conductivity increases at first with dilution, and for many electrolytes attains a limiting value in a dilution of 10,000 litres (p. 256). Arrhenius accounted for this increase on the assumption that the solute consists of "active" and "inactive" parts, and that only the active parts, the ions, convey the current. The extent to which the solute is split up into ions increases with the dilution until finally (when the molecular

conductivity has attained its maximum value) it is completely ionized or completely "active" as far as the conduction of electricity is concerned.

The theory of Arrhenius is based upon the views of Clausius on conductivity, as has already been pointed out. Arrhenius, however, went much further, inasmuch as he showed how, from the results of conductivity and of osmotic pressure measurements, the degree of dissociation can be calculated, as shown in the following section.

Degree of Ionization from Conductivity and Osmotic Pressure Measurements—According to the theory of electrolytic dissociation, the conductivity of a solution depends only on the number of the ions per unit volume, on their charges (which are the same for equivalent amounts of different electrolytes) and on their speed. For the same electrolyte we may assume that the velocities remain practically unaltered on dilution (the friction in a dilute solution being practically the same as that in pure water), therefore the increase of molecular conductivity with dilution must depend almost entirely on an increase in the number of the ions. The molecular conductivity at infinite dilution is given by the formula

$$\mu_{\infty} = u + v,$$

where u and v are the speeds of cation and anion respectively, and the molecular conductivity at any dilution, v, must therefore be represented by the formula

$$\mu_v = \alpha(u + v),$$

where α represents the fraction of the molecules split up into ions. Hence, dividing the second equation by the first, we have

$$\alpha = \frac{\mu_v}{\mu_{\infty}},$$

that is, *the degree of dissociation*, α, *at any dilution, is the ratio of the molecular conductivity at that dilution to the molecular conductivity at infinite dilution.* For example, μ_v for molar sodium chloride is 74·3 and $\mu_{\infty} = 109{\cdot}0$, hence $\alpha = \mu_v/\mu_{\infty} = 74{\cdot}3/109{\cdot}0 = 0{\cdot}682$. Hence sodium chloride in molar solution is about two-thirds split up into its ions.

We have now to consider the deduction of the degree of dissociation from osmotic measurements. The assumption made in this case is that the osmotic pressure is proportional to the number of particles present, the ions acting as separate entities. If a molecule is partially dissociated into n ions and the degree of dissociation—the ionized fraction—is a, then the number of molecules will be $1 - a$, and the number of ions na. Hence the ratio of the number of particles actually present to that deduced according to Avogadro's hypothesis (van't Hoff's factor i) will be

$$i = 1 - a + na = 1 + (an - 1),$$

$$\text{or } a = \frac{i - 1}{n - 1}.$$

As an illustration, de Vries obtained for a 0·14 molar solution of potassium chloride $i = 1{\cdot}81$, hence, since $n = 2$, $a = 0{\cdot}81$, or the salt is dissociated to the extent of 81 per cent. into its ions. i for a 0·18 molar solution of calcium nitrate is 2·48, therefore, since $n = 3$, $a = \frac{1{\cdot}48}{2} = 0{\cdot}74$ in this case.

The agreement in the values of i obtained from conductivity and osmotic measurements is strikingly shown in the accompanying table (van't Hoff and Reicher, 1889). The values of i (osmotic) are from the results of de Vries, those of i (freezing-point) mainly from the observations of Arrhenius, and those of i (conductivity) are calculated by means of the formulæ $a = \mu_v/\mu_\infty$ and $i = 1 + a(n - 1)$ as explained above. It is not certain that the results obtained by the different methods can be expected to agree absolutely (*cf.* p. 287).

Substance.	Concentration (gram-equiv. per litre).	i (freezing-pt.).	i (osmotic).	i (conductivity).
KCl	0·14	1·82	1·81	1·86
LiCl	0·13	1·94	1·92	1·84
$Ca(NO_3)_2$	0·18	2·47	2·48	2·46
$MgCl_2$	0·19	2·68	2·79	2·48
$CaCl_2$	0·184	2·67	2·78	2·42

As regards the mode of ionization, it is clear that univalent compounds, such as potassium chloride, can ionize only in one

way, thus, $KCl \rightleftarrows K^{\cdot} + Cl'$. For more complex molecules, however, there are other possibilities, thus calcium chloride may ionize as follows: $CaCl_2 \rightleftarrows CaCl^{\cdot} + Cl'$ as well as in the normal way $CaCl_2 \rightleftarrows Ca^{\cdot\cdot} + 2Cl'$. If ionization were complete according to the last equation, i would be $= 3$, as compared with the observed value, 2·67 for 0·184 normal solution, given in the table. Similarly, sulphuric acid may dissociate according to the equation $H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4'$, the latter ion then undergoing further ionization as follows: $HSO_4' \rightleftarrows H^{\cdot} + SO_4''$.

Effect of Temperature on Conductivity—The conductivity of electrolytes increases considerably with rise of temperature. The temperature coefficient for salts is 0·020 to 0·023, for acids and some acid salts 0·009 to 0·016, for caustic alkalis about 0·020, and does not vary much with dilution. Conductivity data are usually given for 18°, and the specific conductivity, κ, at any other temperature, is given by the formula

$$\kappa_t = \kappa_{18}[1 + c(t - 18)]$$

where c is the temperature coefficient.

As the conductivity of an electrolyte depends both on the number and velocity of the ions, the question arises as to whether the change of conductivity with temperature is due to the alteration of only one or of both these factors. The matter can be at once decided by calculating the degree of dissociation at the higher temperature from conductivity measurements in the ordinary way, and comparing with that at the lower temperature. For normal sodium chloride at 50°, the value of $a = \mu_v/\mu_\infty = 132/203{\cdot}5 = 0{\cdot}65$, which is only slightly less than the value at 18°, 0·682. Hence, as the considerable increase of conductivity with temperature cannot be due to an increase in the number of ions, it must be due to an increase in their speed. This increased velocity is doubtless connected with the diminution in the internal friction of the medium with rise of temperature, and the consequent diminished resistance to the passage of the ions (p. 258).

Basicity of Acids from Conductivity Measurements (Empirical)—The conductivity of N/32 and N/1024 solutions (equivalent normal) of the sodium salt of the acid is determined. For

monobasic acids the difference $\Lambda_{1024} - \Lambda_{32}$ is about 10, for dibasic acids about 20, and so on (Ostwald).

Grotthus' Hypothesis of Electrolytic Conductivity—Long before the establishment of the electrolytic dissociation theory, Grotthus put forward a hypothesis to account for the conductivity of electrolytes which is of considerable historical interest. He assumed that under the influence of the charged electrodes the molecules of the salt, *e.g.*, potassium chloride, arrange themselves in lines between the electrodes so that the potassium atoms are all turned to the negative electrode, and the chlorine atoms to the positive electrode. Electrolysis takes place in such a way that the external potassium atom is liberated at the cathode and the chlorine atom at the anode. The potassium atom which is left free at the anode unites with the chlorine atom of the molecule next to it, the chlorine atom of the latter with a potassium atom of the molecule next in the chain, and so on. A similar process takes place starting at the anode, in other words, an exchange of partners takes place right along the chain, from one electrode to the other. Under the influence of the charged electrodes, the new molecules twist round till they are in the former relative position, when the end atoms are again discharged, and so electrolysis proceeds.

The fatal objection to this ingenious theory is that a considerable E.M.F. would have to be employed before any decomposition whatever takes place, hence Ohm's law would not hold (*cf.* p. 247).

Practical Illustrations—The following experiments, which are fully described in the course of the chapter, may readily be performed by the student :—

(1) Experiment on the migration velocity of the ions (p. 252).

(2) Rough determination of the absolute velocity of the MnO_4' ion (p. 260).

(3) Determination of the constant of conductivity vessel with $n/50$ potassium chloride. (The specific conductivity, κ, of this solution at different temperatures is as follows : 0·001522 at 0°, 0·001996 at 10°, 0·002399 at 18°, and 0·002768 at 25°.)

(4) Determination of the specific and molecular conductivities of solutions of sodium chloride and of succinic acid.

As the conductivity of solutions varies greatly with the tem-

perature, the conductivity vessel must be partially immersed in a thermostat while measurements are being made.

In the case of sodium chloride, measurements may be made with *n*/1, *n*/10 and *n*/100 solutions, and the values obtained for the molecular conductivity compared with those given in Kohlrausch's tables.[1] The results in very dilute solutions are not trustworthy unless great attention is paid to the purification of the water used in making up the solutions.

In the case of succinic acid, it is usual to start with a 1/16 *molar* solution; 20 c.c. of this solution is placed in the conductivity cell in the thermostat, and when the temperature is constant the resistance is determined. 10 c.c. of the solution is then removed with a pipette, 10 c.c. of water at the same temperature added, the resistance again determined after thoroughly mixing the solution, and so on. Measurements are thus made in dilutions of 16, 32, 64, 128, 256, 512, and 1024 litres. From the values of μ_v thus obtained, the degree of dissociation can be calculated by the usual formula $\alpha = \mu_v/\mu_\infty$. μ_∞ in this case can only be determined indirectly; its value at 25° is about 381. From the values of α in different dilutions, κ, the dissociation constant of the acid may then be calculated; according to Ostwald, K = 0·000066 at 25°.

[1] Full details of electrical conductivity measurements and a large amount of conductivity data are given by Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, Leipzig, 1898.

CHAPTER XI

EQUILIBRIUM IN ELECTROLYTES. STRENGTH OF ACIDS AND BASES. HYDROLYSIS.

The Dilution Law—In a previous chapter it has been shown that chemical equilibria, both in gaseous and liquid systems, can be represented satisfactorily by means of the law of mass action. We have now to apply this law to binary electrolytes, on the assumption that the ions are to be regarded as independent entities.

According to the electrolytic dissociation theory, an aqueous solution of acetic acid contains molecules of non-ionized acid in equilibrium with its ions, represented by the equation



$$CH_3COO' + H^{\cdot} \rightleftarrows CH_3COOH.$$

Suppose in the volume v of solution the total amount of the acid is 1, and that a fraction of it, represented by a, is split up into ions. The concentration of the undissociated acid is $\frac{1-a}{v}$, that of each of the ions (since they are necessarily present in equivalent amount) $\frac{a}{v}$. Hence, from the law of mass action,

$$\left(\frac{a}{v}\right)^2 = K\left(\frac{1-a}{v}\right) \text{ or } \frac{a^2}{(1-a)v} = K \quad . \quad . \quad (1)$$

where K, as before, is the equilibrium constant. For conductivity measurements, the above formula may be put in a rather different form by substituting μ_v/μ_∞ for a. It then becomes

$$\frac{\mu_v^2}{\mu_\infty(\mu_\infty - \mu_v)v} = K.$$

It is preferable, however, to remember the dilution formula in the first form, or in the form $\alpha^2c/(1 - \alpha) = K$.

This relationship, which is known as Ostwald's dilution law, may be tested by substituting a value for α (from conductivity or osmotic observations) at any dilution v, and calculating K, the equilibrium constant; the value of α at any other dilution may then be obtained from the formula and compared with that determined directly. This was done (from conductivity measurements) by van't Hoff and Reicher, and the results are given in the accompanying table :—

Acetic acid : $K = 0{\cdot}0000178$ at $14{\cdot}1°$; $\mu_\infty = 316$.

v (in litres) . .	0·994	2·02	15·9	18·1	1500	3010	7480	15000
μ_v . . .	1·27	1·94	5·26	5·63	46·6	64·8	95·1	129
100α (observed) .	0·40	0·614	1·66	1·78	14·7	20·5	30·1	40·8
100α (calculated) .	0·42	0·6	1·67	1·78	15·0	20·2	30·5	40·1

The agreement between observed and calculated values is excellent; it is, in fact, much closer than for any case of ordinary dissociation so far investigated. The table also shows how small is the dissociation of acetic acid solutions under ordinary conditions; a molar solution is ionized only to the extent of 0·4 per cent., and even a 1/1500 molar solution rather less than 15 per cent.

The dilution law holds for nearly all organic acids and bases, but does not hold for salts, or for certain mineral acids and bases. The latter point is discussed in a later section.

When the degree of dissociation is small, as in the case of acetic acid for fairly concentrated solution, α can be neglected in comparison with 1, and the dilution law then becomes

$$\frac{\alpha^2}{v} = K \text{ or } \alpha = \sqrt{Kv} \quad . \quad . \quad . \quad (2)$$

that is, *for weak electrolytes the degree of dissociation is approximately proportional to the square root of the dilution.* When α cannot be neglected in comparison with 1, α is given by the equation

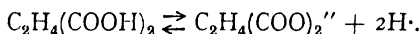
$$\alpha = -\frac{Kv}{2} + \sqrt{Kv + \frac{K^2v^2}{4}} \quad . \quad . \quad . \quad (3)$$

obtained by solving equation (1) for α. In order to familiarize himself with the use of the dilution formula, the student should calculate α for acetic acid in different dilutions from the value of K given above both by the approximate and accurate formula.

The physical meaning of the constant K will be clear if α in the dilution formula (1) is put $= \frac{1}{2}$. Then $2K = 1/v$, that is, 2K is the reciprocal of the volume at which the electrolyte is dissociated to the extent of 50 per cent. Acetic acid, for instance, will be half dissociated at a dilution of

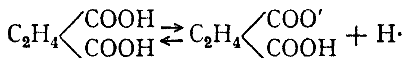
$$\frac{1}{2 \times 0{\cdot}000018} = 27{,}777 \text{ litres } (cf. \text{ table}).$$

As the method of deriving it indicates, the dilution law applies only to binary electrolytes, *i.e.*, electrolytes which split up into two ions only, and it is not therefore *a priori* probable that it will hold for dibasic acids, such as succinic acid, which presumably dissociate according to the equation



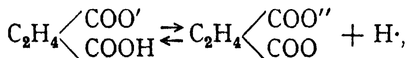
$$C_2H_4(COOH)_2 \rightleftarrows C_2H_4(COO)_2'' + 2H^{\cdot}.$$

It is, however, an experimental fact that when the concentration of succinic acid is expressed in mols (not in equivalents) per litre, the values of K obtained by substitution in the dilution formula remain constant through a wide range of dilution. This indicates that the acid at first splits up into two ions only, doubtless according to the equation



$$C_2H_4\langle{}^{COOH}_{COOH} \rightleftarrows C_2H_4\langle{}^{COO'}_{COOH} + H^{\cdot}$$

and that the second possible stage, represented by the equation

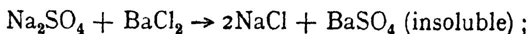


$$C_2H_4\langle{}^{COO'}_{COOH} \rightleftarrows C_2H_4\langle{}^{COO''}_{COO} + H^{\cdot},$$

is not appreciable under the conditions of the experiment. In other cases, however, *e.g.*, fumaric acid, the value of K increases with dilution before the dilution has progressed very far, which indicates that the second stage of the dissociation early becomes of importance.

Strength of Acids—We are accustomed to estimate the strength of acids in a roughly qualitative way by their relative displacing

power. Sulphuric acid, for example, is usually regarded as a strong acid, because it can displace such acids as acetic and hydrocyanic from combination. This principle can be developed to a quantitative method for estimating the relative strengths of acids (and bases) if care is taken to make the comparison under proper conditions. This is sufficiently secured *by making the experiments in a homogeneous system under such conditions that all the reacting substances and products of reaction remain in the system.* We learn in studying inorganic chemistry that many reactions proceed wholly or partially in a particular direction for two main reasons: (*a*) because an insoluble (or practically insoluble) product is formed which is thus removed from the reacting system, *e.g.*,



$$Na_2SO_4 + BaCl_2 \rightarrow 2NaCl + BaSO_4 \text{ (insoluble)};$$

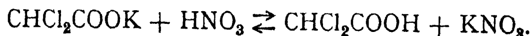
(*b*) because a volatile product is formed which under the conditions of experiment leaves the reacting system, *e.g.*,



$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl \text{ (volatile)}.$$

Such reactions are obviously unsuitable for determining the relative strengths of the acids concerned.

Bearing these considerations in mind, we now proceed to investigate the relative strengths of, say, nitric and dichloracetic acids by bringing them in contact with an amount of base insufficient to saturate both of them, and find how the base distributes itself between the two acids. If, for example, the acids are taken in equivalent amount, and sufficient base is taken to saturate one of them, we have to determine the position of equilibrium represented by the equation



$$CHCl_2COOK + HNO_3 \rightleftarrows CHCl_2COOH + KNO_3.$$

It is evident that no chemical method would answer the purpose, because it would disturb the equilibrium. When, however, a physical property of one of the components, which alters with the concentration, can be measured, the position of equilibrium can be determined. A method used for this purpose by Ostwald, depending on the changes of volume on neutralization, will be readily understood from an example.

When a mol of potassium hydroxide is neutralized by nitric

acid in dilute solution, there is an increase of volume of about 20 c.c. When, on the other hand, the same quantity of alkali is neutralized by dichloracetic acid, the increase of volume is about 13 c.c. It is therefore clear that the complete displacement of dichloracetic acid by nitric acid, according to the equation



$$CHCl_2COOK + HNO_3 \rightarrow CHCl_2COOH + KNO_3,$$

would give an increase of volume of $(20 - 13) = 7$ c.c.; if no displacement took place, there would, of course, be no change of volume. The change actually observed was 5·67 c.c., which means that the reaction represented by the equation has gone from left to right to the extent of $\frac{5 \cdot 67}{7 \cdot 0} = 80$ per cent. approximately; in other words, the nitric acid has taken 80 per cent. of the base, and 20 per cent. has remained combined with the dichloracetic acid. The relative strength, or relative activity, of the acids under these conditions is therefore 80 : 20 or 4 : 1.

Any other physical property, which is capable of quantitative measurement and differs for the two systems, can be equally well employed for the determination of equilibrium. The heat of neutralization has been used for this purpose by Thomsen, and the measurement of the refractive index by Ostwald; the principle of the methods is exactly the same as in the example just given.

Thomsen's thermochemical measurements were the first to be made on this subject, and he arranged the different acids in the order of their "avidities" or activities. Ostwald then showed that the same order of the avidities was obtained by the volume and refractivity methods, and, further, that the results were independent of the nature of the base competed for, so that the avidities are specific properties of the acids.

The relative strength of acids can also be determined on an entirely different principle, depending on kinetic measurements. It has already been pointed out that acids accelerate, in a catalytic manner, the hydrolysis of cane sugar, of methyl acetate, acetamide, etc. Ostwald made many experiments on this subject and reached the very important conclusion that the order of the activity of acids is the same, whether measured by the

distribution method (which is, of course, a static method), or by a kinetic method. This affords further evidence in favour of the conclusion just mentioned, that *the activity or affinity is a specific property of the particular acid, independent of the method by which it is measured.*

Thus far had our knowledge of the subject progressed when in 1884 the first paper of Arrhenius appeared. He showed that *the order of the "strengths" of the acids as determined by the methods just described is also that of their electrical conductivities in equivalent solution.* This fundamentally important fact is illustrated in the accompanying table, in which the conductivities of the acids in normal solution are quoted, that of hydrochloric acid being taken as unity.

Acid.	Relative Activity. Thermochemical.	Cane Sugar.	Conductiv
Hydrochloric	100	100	100
Nitric	100	100	99·6
Sulphuric	49	53·6	65·1
Monochloracetic	9	4·8	4·9
Acetic	—	0·4	1·4

We have seen that, according to the electric dissociation theory, the electrical conductivity of an acid is mainly determined by its degree of dissociation; for example, the conductivity of a normal solution of acetic acid is small because it is ionized only to a very small extent. Further, owing to the predominant share taken by the hydrogen ions in conveying the current (p. 258), the relative conductivities of acids will be approximately proportional to their H· ion concentrations. It is therefore natural to suppose that *the activity of acids, as illustrated by distribution and catalytic effects, is also due to that which all acids have in common, namely, hydrogen ions.* This assumption is in complete accord with the experimental results, as the following illustration shows. The velocity constant for the hydrolysis of cane sugar in the presence of 1/80 normal hydrochloric acid is 0·00469 at 54·3° (time in minutes); as the acid may be regarded as completely dissociated $C_{H\cdot} =$ 0·0125. $C_{H\cdot}$ for 1/4 normal acetic acid ($v = 4$, *cf.* p. 273) may be calculated from the dilution formula or directly from the equilibrium equation as follows :—

$$\frac{[H\cdot][CH_3COO']}{[CH_3COOH]} = \frac{[H\cdot]^2}{[CH_3COOH]} = \frac{[H\cdot]^2}{[0\cdot25 - H\cdot]} = 0\cdot00001615,$$

whence $C_{H\cdot} = 0\cdot002$.

On the assumption that the catalytic effect of acids is proportional to the H· ion concentration, the value of the velocity constant, x, for the hydrolysis of cane sugar by 0·25 normal acetic acid at 54·3° should be

$$0\cdot0125 : 0\cdot00469 :: 0\cdot002 : x,$$

whence $x = 0\cdot00075$. This is identical with the result obtained experimentally by Arrhenius, and we have here a very striking confirmation of the electrolytic dissociation theory.

From the above considerations, we conclude that the characteristic properties which acids have in common, such as sour taste, action on litmus, catalytic activity, property of neutralizing bases, etc., are due to the presence of H· ions. It must be remembered that *direct* proportionality between H· ion concentration and conductivity is neither observed nor to be expected from the theory; the *approximate* proportionality is due to the great velocity of the hydrogen ions, and would be altogether absent if the anions were the more rapid.

As there is a simple relationship between the H· ion concentration of weak acids and their dissociation constants (p. 273), it is clear that the behaviour of an acid can be to a great extent foretold when its dissociation constant has been measured. Such determinations have been made for a great number of weak acids by Ostwald and others, and some of the results are given in the accompanying table, which shows very clearly how greatly the value of K differs for different acids, and the influence of substitution :—

Acid.	Value of K at 25° (v in *litres*).	
Acetic $H\cdot CH_3COO$	0·000018 =	$180{,}000 \times 10^{-10}$
Monochloracetic $H\cdot CH_2ClCOO$	0·00155	—
Trichloracetic $H\cdot Cl_3COO$	1·21	—
Cyanacetic $H\cdot CH_2CNCOO$	0·0037	—
Formic $H\cdot HCOO$	0·000214	—
Carbonic $H\cdot HCO_3$	—	3040×10^{-10}
Hydrogen sulphide $H\cdot SH$	—	570×10^{-10}
Hydrocyanic $H\cdot CN$	—	13×10^{-10}
Phenol $H\cdot OC_6H_5$	—	$1\cdot3 \times 10^{-10}$

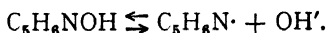
For a weak acid, $\alpha = \sqrt{Kv}$, where α is the degree of dissociation at the volume v. Hence, for two acids at the same dilution $\alpha/\alpha' = \sqrt{K/K'}$, or the ratio of the degrees of dissociation is equal to the square root of the ratio of the dissociation constants. From the data given in the table it can readily be calculated that in solutions of monochloracetic and acetic acid of the same concentration the ratio of the H· ion concentrations is approximately 9·3 : 1. The effect of replacing one of the hydrogens in acetic acid by chlorine is thus to form a much stronger acid and the CN group has a still greater effect, as the table shows.

A further important point is the effect of dilution on the "strength" of an acid. As the degree of dissociation increases regularly with dilution, it is evident that the activity of a weak acid will approach nearer and nearer to that of a strong acid (which is completely active in moderate dilution) until finally, when the weak acid is completely ionized, it will have the same strength as the strong acid in equivalent dilution. It follows that the strength of acids is the more nearly equal the more dilute the solution, and that at "infinite dilution" all acids are equally strong. It can readily be calculated from the conductivity tables that the relative strengths of hydrochloric and acetic acids in different dilutions are as follows :—

Concentration	$n/1$	$n/10$	$n/100$	$n/1000$	$n/10,000$
α for HCl . .	0·81	0·91	0·97	0·99	1·0
α for $HC_2H_3O_2$.	0·004	0·013	0·04	0·13	0·4
Ratio $HCl/HC_2H_3O_2$	200	70	24	7·5	2·5

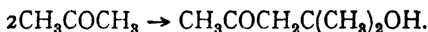
Strength of Bases.—Just as the strength of acids depends on their concentration in hydrogen ions, so the strength of bases depends on the concentration in hydroxyl ions. On this view, potassium hydroxide is a strong base, because in moderate dilution it is almost completely ionized according to the equation $KOH \rightleftarrows K^{\cdot} + OH'$; ammonium hydroxide, on the other hand, is a weak base, because its aqueous solution contains only a relatively small concentration of OH′ ions. Since certain organic compounds, including amines and alkaloids, have basic properties, their aqueous solutions must also contain OH′ ions. Thus, solutions of pyridine, C_5H_5N, contain not only the free

base, but a certain concentration of $C_5H_6N\cdot$ and OH′ ions, in equilibrium with the undissociated hydrate, as represented by the equation



$$C_5H_6NOH \rightleftarrows C_5H_6N\cdot + OH'.$$

The strength of bases may be determined by distribution or catalytic methods, corresponding with those already described for determining the strength of acids, as well as by conductivity methods. A fairly satisfactory catalytic method is the effect on the rate of condensation of acetone to diacetonyl alcohol,[1] represented by the equation



$$2CH_3COCH_3 \rightarrow CH_3COCH_2C(CH_3)_2OH.$$

The order of the strength of bases as determined by this method agrees with the results of conductivity measurements. Another method, which is not purely catalytic, since the base is used up in the process, is the effect on the hydrolysis or saponification of esters (p. 215). This process is usually represented by the typical equation



$$CH_3COOC_2H_5 + KOH = CH_3COOK + C_2H_5OH.$$

Experience shows, however, that for the so-called strong bases, which are almost completely ionized in moderate dilution, the rate of hydrolysis is practically independent of the nature of the cation (whether K, Na, Li, etc.), a fact which is readily accounted for on the view that the ions exist free in solution, as the ionic theory postulates, and that the OH′ ions are alone active in saponification. The general equation for the hydrolysis of ethyl acetate by bases may, therefore, be written as follows:—



$$CH_3COOC_2H_5 + OH' = CH_3COO' + C_2H_5OH.$$

The relative strength of bases, as obtained from their efficiency in saponifying esters, is in excellent agreement with their strength as deduced from conductivity measurements. The ionization view of the saponification of esters is further supported by the fact that the reaction between ethyl acetate and

[1] Koelichen, *Zeitsch. Physikal. Chem.*, 1900, **33**, 129.

barium hydroxide is bimolecular and not trimolecular, as would be anticipated if it proceeded according to the equation



$$2CH_3COOC_2H_5 + Ba(OH)_2 = (CH_3COO)_2Ba + 2C_2H_5OH.$$

The alkali and alkaline earth hydroxides are very strong bases, being ionized to about the same extent as hydrochloric acid in equivalent dilution. Bases differ as greatly in strength as do acids; the dissociation constants for a few of the more important are given in the table :—

Base.	Value of K (25°) (*v* in *litres*).	
Ammonia $NH_4 \cdot OH$	0·000023 =	$230{,}000 \times 10^{-10}$
Methylamine $CH_3NH_3 \cdot OH$	0·00050	—
Trimethylamine $(CH_3)_3NH \cdot OH$	0·000074	—
Pyridine $C_5H_6N \cdot OH$	—	23×10^{-10}
Aniline $C_6H_5NH_3 \cdot OH$	—	$4 \cdot 6 \times 10^{-10}$

Interesting results have been obtained as to the effect of substitution on the strength of bases. Thus the table shows that the basic character is increased by replacing one of the hydrogen atoms in ammonia by the CH_3 group, but is greatly diminished by the C_6H_5 group.

Mixture of two Electrolytes with a Common Ion—The dissociation of weak acids and bases is greatly diminished by the addition of a salt with an ion common to the acid or base. For example, the equilibrium in a solution of acetic acid is represented by the equation $[H^{\cdot}][CH_3COO'] = K[CH_3COOH]$, and if by adding sodium acetate the CH_3COO' ion concentration is greatly increased, the $H^{\cdot}$ ion concentration must correspondingly diminish, since the concentration of the undissociated acid cannot be greatly altered (nearly the whole of the acid being present in that form in the original solution) and therefore the right-hand side of the equation is practically constant.

The exact equations representing the mutual influence of electrolytes with a common ion are somewhat complicated, but an approximate formula which is often useful can be obtained as follows: If the total concentration of a binary electrolyte is c and its degree of dissociation is a, we have, from the law of mass action,

$$(ac)(ac) = K \quad . \quad . \quad . \quad . \quad (1)$$

If now an electrolyte with a common ion is added, and the concentration of the latter is c_o, the above equation becomes

$$\frac{(\alpha' c)(\alpha' c + c_o)}{(1 - \alpha')c} = K \quad . \quad . \quad . \quad (2)$$

This equation is quite accurate. As K, c, and c_o are known, α', where α' is the new degree of dissociation, can be calculated, perhaps most readily by successive approximations.

If the degree of dissociation of the first electrolyte is small, $1 - \alpha'$ can be taken as unity without appreciable error; further, if the second electrolyte is highly ionized and is added in considerable proportion, $\alpha' c$ can be neglected in comparison with c_o, and equation (2) simplifies to

$$(\alpha' c)c_o = Kc \quad . \quad . \quad . \quad . \quad (3)$$

Otherwise expressed, *the concentration of one of the ions of a weak electrolyte is inversely proportional to the ionic concentration of a highly-dissociated salt having an ion in common with the other ion of the weak electrolyte.*

As an illustration of the application of the last equation, we will consider the effect of the addition of an equivalent amount of sodium acetate on the strength of 0·25 molar acetic acid. In this dilution α for the acid is 0·0085 and $\alpha c = 0{\cdot}0085 \times 0{\cdot}25 = 0{\cdot}0021 = C_{H^{\cdot}}$. In 0·25 molar solution, sodium acetate is dissociated to the extent of 69·2 per cent., hence $c_o = 0{\cdot}25 \times 0{\cdot}692 = 0{\cdot}173$. We have, therefore,

$$\alpha' \times 0{\cdot}173 = 0{\cdot}000018, \text{ whence } \alpha' = 0{\cdot}0001.$$

α'c is therefore $0{\cdot}25 \times 0{\cdot}0001 = 0{\cdot}000025 = C_{H^{\cdot}}$ in presence of 0·25 molar sodium acetate, so that the strength of the acid is diminished in the ratio 85 : 1. In an exactly similar way, the strength of ammonia as a base is greatly reduced by the addition of ammonium salts.

This action of neutral salts on weak bases and acids is largely taken advantage of in analytical chemistry. For example, the concentration of OH′ ions in ammonia solution is sufficient to precipitate magnesium hydroxide from solutions of magnesium salts, but in the presence of ammonium chloride the OH′ ion

concentration is so greatly reduced that precipitation no longer occurs. Similarly, the addition of hydrochloric acid diminishes the concentration of S″ ions in hydrogen sulphide to such an extent that zinc salts are no longer precipitated (*cf.* p. 305).

Isohydric Solutions—It is of particular interest to inquire what must be the relation between two solutions with a common ion—two acids, for example—in order that, when mixed, they may exert no mutual influence. This problem was investigated both theoretically and practically by Arrhenius, who showed that no alteration in the degree of dissociation of either of the salts (acids or bases) takes place when the concentration of the common ion in the two solutions before mixing is the same. Such solutions are termed *isohydric.*

The proof of the conditions under which two solutions are isohydric is as follows: Suppose the electrolytes with a common ion are two monobasic acids, HA and HA′, both of which obey Ostwald's dilution law, and that in isohydric solutions of the two acids the dilutions are v and v' and the degrees of dissociation a and a' respectively. For the acid HA, according to the law of mass action, the equation holds

$$\frac{a^2}{(1-a)v} = K \quad . \quad . \quad . \quad . \quad (1)$$

and for the acid HA′ the corresponding equation

$$\frac{a'^2}{(1-a')v'} = K' \quad . \quad . \quad . \quad . \quad (2)$$

When the solutions are mixed, the volume becomes $v + v'$ and the proportion of H′ ions $a + a'$. For the acid HA we now have

$$\frac{a(a+a')}{(1-a)(v+v')} = K \quad . \quad . \quad . \quad (3)$$

Dividing equation (3) by equation (1) we obtain

$$\frac{(a+a')v}{(v+v')a} = 1 \text{ or } \frac{a+a'}{a} = \frac{v+v'}{v}$$

whence

$$\frac{a'}{a} = \frac{v'}{v} \text{ or } \frac{a}{v} = \frac{a'}{v'}.$$

Now a/v and a'/v' are the respective concentrations of H· ions in the isohydric solutions of the acids and have now been shown to be equal—in other words, the condition for isohydry is that the concentration of the common ion in the two solutions before mixing must be the same.

The relative dilutions in which two acids or other electrolytes with a common ion are isohydric can readily be calculated from their dissociation constants. The value of K for acetic acid is 0·000018, and for cyanacetic acid 0·0037, both at 25°. Since $\alpha = \sqrt{Kv}$ approximately, it is clear that the degree of dissociation, α, will be the same for the two acids when the dilutions are inversely as the dissociation constants. The dilution of the cyanacetic acid must therefore be 3700 : 18, or 205 times that of acetic acid for isohydric solutions.

Arrhenius has shown that by the principle of isohydric solutions the mutual influence of electrolytes with a common ion even of strong acids and their neutral salts, can be calculated with a considerable degree of accuracy, but the methods are somewhat complicated and cannot be given here. Not only is the degree of dissociation of a weak acid greatly influenced by the addition of a strong acid, or other electrolyte with a common ion, but the latter is affected, though to a much smaller extent, by the presence of the former. It can, for instance, be calculated that when a mol of acetic acid and a mol of cyanacetic acid are present in a litre of water, the dissociation of the former is only about 1/14 of its value in aqueous solution, whilst the presence of the acetic acid only diminishes the dissociation of the cyanacetic acid by 0·25 per cent.

Mixture of Electrolytes with no Common Ion—The equilibrium in a mixture of two electrolytes without a common ion can be calculated when the concentrations and dissociation constants are known, but the calculation is somewhat complicated. If solutions of two highly-dissociated salts, such as potassium chloride and sodium bromide, are mixed, small amounts of undissociated sodium chloride and potassium bromide will be formed; but as the salts are all highly dissociated, the mutual effect is very small. If dissociation is complete, the process will be represented by the equation



$$K^{\cdot} + Cl' + Na^{\cdot} + Br' = K^{\cdot} + Cl' + Na^{\cdot} + Br',$$

otherwise expressed, the salts will exert no mutual influence. These considerations account for the observation of Hess (p. 153) that the thermal effect of mixing dilute solutions of two binary salts is very slight. At the time Hess made his observation, it was extremely puzzling, because it was known that the heats of formation of different salts were very different, and therefore heat should either be absorbed or given out as an accompaniment of the double decomposition. On the basis of the electrolytic dissociation theory, however, Hess's results at once become intelligible, since both before and after admixture the solution contains mainly the same free ions.

To the question which is very often asked as to what compounds are present in a mixed salt solution, it must therefore be answered that all the undissociated salts and ions are present which can be formed by interaction of the components, and that the proportions in which the various molecules and ions are present depend on the concentrations and dissociation constants of the various salts.

Dissociation of Strong Electrolytes[1]—It has been pointed out (p. 273) that the law of mass action holds for weak (*i.e.*, slightly ionized) electrolytes, the ions being regarded as independent units. The proof of the applicability of the law has been brought more particularly by Ostwald from the results of measurements with organic acids. It is a remarkable fact, however, that the dilution formula, $\alpha^2/(1 - \alpha)v = K$, which is a direct consequence of the law of mass action, does not appear to be valid for the so-called "strong" or highly dissociated electrolytes; when the values of α, obtained from osmotic or conductivity measurements, are substituted in the above formula, K diminishes greatly with dilution. This is well shown in the following table for silver nitrate. The first column contains v, the volume in litres in which 1 mol of the salt is dissolved, in the second column is given the value of α calculated from conductivity measurements at 25°, and in the third column are given the values of K calculated by means of the dilution formula.

[1] *Cf.* General Discussion, *Trans. Faraday Society*, 1919, **15**.

v.	$a = \mu_v/\mu_\infty$.	K.	K_1.
16	0·8283	0·253	1·11
32	0·8748	0·191	1·16
64	0·8993	0·127	1·06
128	0·9262	0·122	1·07
256	0·9467	0·124	1·08
512	0·9619	0·125	1·09

The deviations from the simple law appear to be fairly regular in character, and van't Hoff has proposed an empirical formula which represents with a fair degree of accuracy the behaviour of the great majority of strong electrolytes. The formula in question is of the form

$$a^3/(1 - a)^2 v = K_1$$

which may also be written

$$C_i^3/C_u^2 = K_1$$

where C_i represents the concentration of the dissociated part (the ions), C_u that of the undissociated part. The application of this formula to solutions of silver nitrate is illustrated in the table, and it will be observed that the values of K_1 in the fourth column are fairly constant. The slightly different formula suggested by Rudolphi

$$\frac{a^2}{(1 - a)\sqrt{v}} = K_2$$

is scarcely as satisfactory as that of van't Hoff. Some observers have suggested a generalized form of van't Hoff's formula,[1] as follows :—

$$C_i^n/C_u = K_3$$

and experiment shows that in many cases n does not differ much from 1·5. When n is 1·5 the general formula reduces to that of van't Hoff.

The reason why the law of mass action does not apply to strong electrolytes, although it holds so accurately for weak electrolytes, has not been satisfactorily elucidated. It was long

[1] *Cf.* Bancroft, *Zeitsch. Physikal. Chem.*, 1899, **31**, 188.

thought that the values of α obtained from the results of conductivity measurements were not the true values of the degree of dissociation, but recent very careful comparison shows that the results obtained by conductivity and freezing-point determinations in dilute solution for the best-investigated substances do not, as a rule, differ by more than 2 per cent. on the average, and even these differences may be due largely to experimental error.[1] In a few cases only does there appear to be a real difference between the results obtained by the two methods. As neither of the values for α gives a constant value for K when substituted in the ordinary dilution formula, there can be no doubt that strong electrolytes do behave in an anomalous way.

Several disturbing causes might be suggested to account for this behaviour, including (*a*) the formation of complex ions by combination of the ions with non-ionized molecules; (*b*) mutual influence of the ions; (*c*) interaction of the ions and the solvent, including more particularly hydration of the ions, and one or more of these effects may be operative in any one solution. The existence of complex ions in solutions has been definitely proved by Hittorf and others. In solutions of cadmium iodide, for instance, there is evidence that I′ ions unite with CdI_2 molecules to form complex ions of the formula CdI_4''. The formation of complex ions would diminish the number of non-ionized molecules but not the total number of ions; it would thus affect the osmotic pressure, but not to any extent the conductivity. This disturbing effect will be greatest in fairly concentrated solutions. In dilute solutions of salts of the alkalis and alkaline earths, the values of α obtained by conductivity and osmotic pressure methods are very nearly equal, and this result appears to show that there is little or no complex ion formation in these solutions.

As to the possible effect of the ions on each other considerable progress has been made. The fact that weak electrolytes follow the law of mass action through a very wide range of dilution is probably connected with the fact that under all circumstances the ionic concentration is small, a condition which no longer holds in solutions of strong electrolytes. The theory

[1] Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454; Lewis and Randall, *loc. cit.*, 1921, **43**, 1112.

of interionic attraction (p. 347) has done much to elucidate the anomalies.

The possiblity of the interaction of the ions with the solvent has been much discussed, but as no general agreement has been reached on the matter, a short reference to the subject here will suffice. One way in which this effect might influence the results would be if the ions became associated with a large proportion of water which no longer acted as solvent. The effective concentrations of an ion would then be the ratio of the amount present to that of the "free" solvent, instead of to the total solvent, as usually calculated. As, however, no satisfactory method of estimating the relative proportions of free and combined solvent in the solution of an electrolyte has yet been suggested the question is at present mainly of theoretical interest (p. 341).

Many years ago Nernst [1] suggested the most logical method of dealing with the problem of strong electrolytes. He considered that, owing to their mutual influence, the activity of the various substances (ions and non-ionized substances) present is not proportional to their respective concentrations, but certain correcting factors have to be applied depending on the extent of the mutual influence. Among these effects, that of the ions on each other and on the non-ionized part of the molecules, as well as the mutual influence between ions and solvent, seemed to be of special importance (p. 347).

Electrolytic Dissociation of Water. Heat of Neutralization—So far we have regarded the usual solvent water simply as a medium for dissociation, but there is evidence to show that it is itself split up to a very small extent into ions, according to the equation

$$H_2O \rightleftarrows H^{\cdot} + OH'.$$

Applying to this equation the law of mass action, we have, as usual,



$$[H^{\cdot}][OH'] = K[H_2O],$$

where K is the *dissociation constant* for water. As the ionic concentrations are extremely small the concentration of the

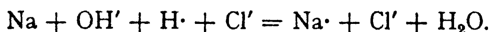
[1] *Zeitsch. physikal. Chem.*, 1901, **36**, 487.

water is practically constant, and therefore the product of the concentration of the ions

$$[H\cdot][OH'] = K_w, \text{ a constant.}$$

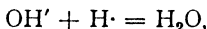
It has been found by different methods, which will be referred to later (p. 298), that the value of the above constant at 25° is about $1{\cdot}2 \times 10^{-14}$. In pure water the concentrations of the ions are necessarily equal, hence $C_H = C_{OH'} = \sqrt{1{\cdot}2 \times 10^{-14}} = 1{\cdot}1 \times 10^{-7}$ at 25°. Otherwise expressed, this means that pure water contains rather more than 1 mol of H· and OH′ ions, that is 1 gram of H· ions and 17 grams of OH′ ions, in 10^7 or 10,000,000 litres. The ionic product is independent of whether the solution is acid or alkaline, and therefore in a normal solution of a (completely dissociated) acid, since $C_{H\cdot} = 1$, $C_{OH'}$ is only 10^{-14}, and in a solution of a normal alkali $C_{H\cdot}$ is correspondingly small.

These considerations are of great importance in connection with the process of neutralization. Assuming that the solutes are completely ionized, the neutralization of 1 mol of sodium hydroxide by hydrochloric acid in dilute solution may be represented as follows :—



$$Na + OH' + H\cdot + Cl' = Na\cdot + Cl' + H_2O.$$

Since Na· and Cl′ ions occur in equivalent amount on each side, they may be neglected, and the equation reduces to



$$OH' + H\cdot = H_2O,$$

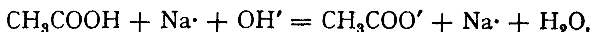
or, otherwise expressed, the combination of hydrogen and hydroxyl ions to form water. The same equation applies to the neutralization of any other strong base by a strong acid; *provided that the solutions are so dilute that dissociation is practically complete, the process in all cases consists in the combination of H· and OH′ ions to non-ionized water.* It may, therefore, be anticipated that for equivalent amounts of different strong bases and acids the heat of neutralization will be the same, and that this is actually the case is shown in the first part of the table. The magnitudes of the heats of neutralization apply for molar quantities.

Heats of Neutralization.

Acid and Base.	Heat of Neutralization.
HCl and NaOH	13,700 cal.
HBr and NaOH	13,700 cal.
HNO_3 and NaOH	13,700 cal.
HCl and $\frac{1}{2}Ba(OH)_2$	13,800 cal.
. . . .	. . . . .
NaOH and CH_3COOH	13,400 cal.
NaOH and HF	16,300 cal.
HCl and ammonia	12,200 cal.
HCl and dimethylamine	11,800 cal.

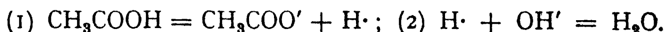
The fact that the heat of neutralization of strong acids and bases is independent of the nature of the acid and base was long a puzzle to chemists, and the simple explanation given above is one of the conspicuous triumphs of the electrolytic dissociation theory.

Below the dotted line in the above table are given the heats of neutralization of two weak acids by a strong base and of two weak bases by a strong acid. As the table shows, the heat development in these cases may be more or less than 13,700 cal. for molar quantities, and a little consideration affords a plausible explanation. The neutralization of acetic acid, which is very slightly ionized, by sodium hydroxide, may be represented by the equation



$$CH_3COOH + Na^{\cdot} + OH' = CH_3COO' + Na^{\cdot} + H_2O,$$

which may be regarded as taking place in two stages—



$$(1)\ CH_3COOH = CH_3COO' + H^{\cdot}\,;\quad (2)\ H^{\cdot} + OH' = H_2O.$$

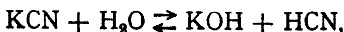
The heat of neutralization is, therefore, the sum of two effects (1) the heat of dissociation of the acid; (2) the reaction $H^{\cdot} + OH' = H_2O$, which gives out 13,700 cal. Hence, since the observed thermal effect is 13,400 cal. the dissociation of the acid must absorb 300 cal. For hydrofluoric acid, on the other hand, the reaction $HF = H^{\cdot} + F'$ is attended by a heat development of $16,300 - 13,700 = 2,600$ cal. We have thus an approximate method of determining the *heat of ionization* of electrolytes, which may be positive or negative.

In the above paragraphs the total heat change has been regarded as the algebraic sum of the heats of neutralization and of ionization, but it is probable that other phenomena, for example, changes of hydration, also play a part.

Hydrolysis—It is a well-known fact that salts formed by a weak acid and a strong base, such as potassium cyanide, show an alkaline reaction in aqueous solution, whilst salts formed by the combination of a weak base and a strong acid, for example, ferric chloride, have an acid reaction. In the previous section it has been mentioned that water is slightly ionized, according to the equation $H_2O = H^{\cdot} + OH'$, and may therefore be regarded as at the same time a weak acid (since $H^{\cdot}$ ions are present) and a weak base (owing to the presence of OH' ions). It will now be shown that the behaviour of aqueous solutions of such salts as potassium cyanide and ferric chloride are *quantitatively* accounted for on the assumption that water is electrolytically dissociated.

In a previous section (p. 275) it has been pointed out that when two acids are allowed to compete for the same base, the latter distributes itself between the acids in proportion to their avidities, and it has also been shown that the ratio of the avidities of two acids is the ratio of the extent to which they are electrolytically dissociated. The same applies to a salt in aqueous solution, *water, in virtue of its hydrogen ion concentration, being regarded as one of the competing acids.* In the case of a salt of a strong acid, such as sodium chloride, it would not be anticipated that such a weak acid as water would take an appreciable amount of the base, and the available experimental evidence quite bears out this expectation. In other words, an aqueous solution of sodium chloride contains only $Na^{\cdot}$ and Cl' ions and undissociated sodium chloride in appreciable amount, and is therefore neutral.

The case is quite different for a salt formed by a strong base and a weak acid, such as potassium cyanide. Here water as an acid is comparable in strength to hydrocyanic acid, and therefore there is a distribution of the base between the acid and the water according to the equation

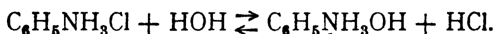


$$KCN + H_2O \rightleftarrows KOH + HCN,$$

the proportions of potassium cyanide and potassium hydroxide depending upon the relative strengths of water and hydrocyanic acid.

From the equation it is evident that potassium hydroxide and hydrocyanic acid must be present in equivalent amount; and since the hydroxide is much more highly ionized that hydrocyanic acid, the solution contains an excess of OH′ ions, and must therefore be alkaline, as is actually the case.

This process is termed *hydrolysis*, *i.e.*, decomposition by means of water. Similar considerations apply to the salts formed by combination of weak bases and strong acids, such as aniline hydrochloride. As water is comparable in strength to aniline as a base, an equilibrium is established according to the equation

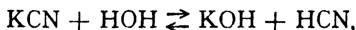


$$C_6H_5NH_3Cl + HOH \rightleftarrows C_6H_5NH_3OH + HCl.$$

In this case there is an excess of H· ions, as hydrochloric acid is much more highly ionized than anilinium hydroxide, and therefore the solution has an acid reaction.

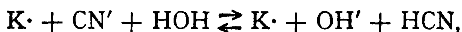
A salt formed by the combination of a weak acid and a weak base, *e.g.*, aniline acetate, is naturally hydrolysed to a still greater extent. These three types of hydrolytic action will now be considered quantitatively.

(*a*) **Hydrolysis of the Salt of a Strong Base and a Weak Acid**—A typical salt of this type is potassium cyanide, the hydrolytic decomposition of which is represented by the equation



$$KCN + HOH \rightleftarrows KOH + HCN,$$

or, according to the electrolytic dissociation theory,



$$K^{\cdot} + CN' + HOH \rightleftarrows K^{\cdot} + OH' + HCN,$$

on the assumption, which is only approximately true, that potassium cyanide is completely ionized and hydrocyanic acid non-ionized.

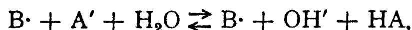
The equilibrium can now be investigated, and the extent of the hydrolysis determined, if a means can be found of determining the equilibrium concentration of one of the reacting substances, for example, the OH′ ions. This could not, of course, be done by titrating the free alkali, as the equilibrium

would thus be disturbed, but one of the methods given on p. 280 may conveniently be used. The method which has been most largely used is to determine the effect of the mixture on the rate of saponification of methyl acetate, which, as has already been pointed out, is proportional to the OH′ ion concentration. The amount of hydrolysis per cent., $100x$, for different concentrations, c, of potassium cyanide (mols per litre) at 25°, determined by the above method, is as follows :—

c . .	0·947	0·235	0·095	0·024
$100x$ . .	0·31	0·72	1·12	2·34
K_h . .	0·9	1·2	1·2	$1·3 \times 10^{-5}$

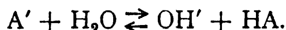
The table shows that, as is to be expected, the degree of hydrolysis increases with dilution.

A general equation, by means of which the equilibrium condition can be calculated when the acid and base are not necessarily present in equivalent proportions, can readily be obtained by applying the law of mass action to the general equation



$$B^{\cdot} + A' + H_2O \rightleftarrows B^{\cdot} + OH' + HA,$$

where $B^{\cdot}$ and A' represent the positive and negative ions respectively. As $B^{\cdot}$ occurs on both sides of the above equation, the latter can be simplified to



$$A' + H_2O \rightleftarrows OH' + HA.$$

As the salt and the base are practically completely ionized, and the acid is not appreciably ionized, A' and OH' are proportional to the concentrations of salt and base respectively, and HA to that of the acid. Hence, from the law of mass action,

$$\frac{[OH'][HA]}{A'} = \frac{[\text{free base}]\,[\text{free acid}]}{[\text{unhydrol. salt}]} = K_h \quad . \quad (1)$$

a constant, as the concentration of the water may be regarded as constant. K_h is termed the *hydrolysis constant*, and, like the ordinary equilibrium constant, is independent of the relative concentrations of the substances present at equilibrium, but depends on the temperature.

In order to illustrate the use of the above formula, the values of K_h may be calculated from the data for potassium cyanide

already quoted. In 0·095 molar solution, potassium cyanide is hydrolysed to the extent of 1·12 per cent., hence

$$C_{base} = C_{acid} = \frac{0{\cdot}095 \times 1{\cdot}12}{100} = 0{\cdot}001064,$$

and

$$C_{salt} = 0{\cdot}095 - 0{\cdot}001064 = 0{\cdot}094.$$

Hence

$$K_h = \frac{(0{\cdot}001064)(0{\cdot}001064)}{0{\cdot}094} = 1{\cdot}2 \times 10^{-5}.$$

The values of the hydrolysis constant, calculated from the other observations, are given in the table, and are approximately constant, thus confirming the above formula. Conversely, when from one set of observations the value of K_h has been obtained, the degree of hydrolysis at any other dilution can be obtained by substitution in the general formula.

For convenience of calculation, the simple formula in which the acid and base are present in equivalent proportions, may be written in the form

$$\frac{x^2}{(1 - x)v} = K_h \quad . \quad . \quad . \quad . \quad (1a)$$

in which x represents the proportion of acid and base formed by hydrolysis from 1 mol of the salt and v is the dilution. This form of the equation shows at a glance that the degree of hydrolysis, that is, the value of x, increases with dilution. Moreover, from the great similarity of the formula (1a) to the dilution formula, it is evident that when the hydrolysis is small it is greatly diminished by the addition of a strong base, just as the degree of dissociation of acetic acid is greatly diminished by the addition of an acetate.

The quantitative relation between the hydrolysis constant, K_h, and the dissociation constants for the weak acid and water respectively may be obtained as follows: The electrolytic dissociation of the acid, HA, is represented by the equation



$$[H^{\cdot}][A'] = K_a[HA] \quad . \quad . \quad . \quad (2)$$

where K_a is the dissociation constant of the acid. In the solution there is the other equilibrium $[H^{\cdot}]\,[OH'] = K_w$ (3)

where K_w is the ionic product for water. Dividing equation (3) by (2) we obtain

$$\frac{[OH'][HA]}{A'} = \frac{K_w}{K_a} \quad . \quad . \quad . \quad (4)$$

The left-hand side of the above equation is simply equation (1) for the hydrolytic equilibrium (p. 293), hence

$$\frac{[\text{free base}]\ [\text{free acid}]}{[\text{unhydrol. salt}]} = K_h = \frac{K_w}{K_a} \quad . \quad . \quad (5)$$

that is, *the hydrolysis constant* K_h *is the ratio of the ionic product* K_w *for water to the dissociation constant of the acid.* It has already been deduced from general principles (p. 291) that the hydrolysis is the greater the more nearly the strength of water as an acid approaches that of the competing acid, and the above important result is the mathematical formulation of that statement.

In order to illustrate this point more fully, the degree of hydrolysis of a few salts in 1/10 molar solution at 25° is given in the accompanying table:—

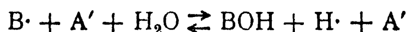
Salt.	Degree of hydrolysis.
Sodium carbonate	3·17 per cent.
Sodium phenolate	3·05 ,,
Potassium cyanide	1·12 ,,
Borax	0·05 ,,
Sodium acetate	0·008 ,,

The numbers illustrate in a very striking way the fact that only the salts of very weak acids are appreciably hydrolysed. Thus although acetic acid is a fairly weak acid ($K = 1{\cdot}8 \times 10^{-5}$), sodium acetate is only hydrolysed to the extent of 0·008 per cent. at 25°, and even potassium cyanide is only hydrolysed to the amount of about 1 per cent. in 1/10 normal solution, although the dissociation constant of the acid is only $1{\cdot}3 \times 10^{-9}$. A comparison of the above table with the dissociation constants of the acids (p. 278) is very instructive. From the known values of K_a and K_w for hydrocyanic acid and water respectively at 25°, we have

$$\frac{K_w}{K_a} = \frac{1{\cdot}2 \times 10^{-14}}{1{\cdot}3 \times 10^{-9}} = 0{\cdot}9 \times 10^{-5} = K_h,$$

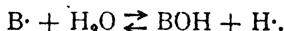
in satisfactory agreement with the observed value of $1 \cdot 2 \times 10^{-5}$ (p. 294). As a matter of fact, however, it is easier to determine the hydrolysis constant than the dissociation constant for a very weak acid, and therefore the latter is often calculated from the observed value of the hydrolysis constant by means of the above formula.

(*b*) **Hydrolysis of the Salt of a Weak Base and a Strong Acid**—The same considerations apply in this case as for the salt of a strong base and a weak acid. The general equation for the equilibrium is of the form



$$B^{\cdot} + A' + H_2O \rightleftarrows BOH + H^{\cdot} + A'$$

which simplifies to



$$B^{\cdot} + H_2O \rightleftarrows BOH + H^{\cdot}.$$

Applying the law of mass action, we obtain

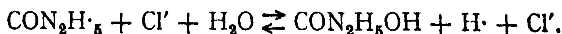
$$\frac{[BOH][H^{\cdot}]}{B^{\cdot}} = \frac{[\text{free base}]\,[\text{free acid}]}{[\text{unhydrol. salt}]} = K_h \quad . \quad (1)$$

exactly the same equation as is applicable to the hydrolysis of the salt of a strong base and a weak acid. Further, it may be shown, by a method exactly analogous to that employed in the previous section, that in this case

$$K_h = \frac{K_w}{K_b} \quad . \quad . \quad . \quad . \quad (2)$$

that is, *the hydrolysis constant* K_h *for the salt of a weak base and a strong acid is the ratio of the ionic product for water*, K_w, *and the dissociation constant of the base*, K_b.

A typical case is the hydrolysis of urea hydrochloride,[1] which may be represented thus—



$$CON_2H^{\cdot}_5 + Cl' + H_2O \rightleftarrows CON_2H_5OH + H^{\cdot} + Cl'.$$

It is clear that the degree of hydrolysis can at once be obtained when the H· ion concentration in the solution has been determined, and for this purpose any of the methods previously described can be employed (p. 276), such as the effect on the

[1] Walker, *Proc. Roy. Soc.* (*Edin.*), 1894, **18**, 255.

rate of hydrolytic decomposition of cane sugar or of methyl acetate or by electrical conductivity measurements. In the experiments quoted in the table, gradually increasing amounts of urea were added to normal hydrochloric acid, and the H· ion concentration deduced from a comparison of the velocity constant for the hydrolysis of cane sugar in the presence of the free acid (k_0), and with the addition of urea (k).

Normal hydrochloric acid + c normal urea.

c.	k.	k/k_0 = free HCl.	$1 - k/k_0$ = salt formed.	$c - 1 + k/k_0$ = free urea.	K_h.
0	0·00315 = k_0	1	—	—	—
0·5	0·00237	0·753	0·247	0·253	0·77
1·0	0·00184	0·585	0·415	0·585	0·82
2·0	0·00114	0·36	0·64	1·36	0·77
4·0	0·0006	0·19	0·81	3·19	0·75

On the assumption that the rate of hydrolytic decomposition is proportional to the H· ion concentration, k/k_0 represents the concentration of the "free" hydrochloric acid, and $(1 - k/k_0)$ that of the bound acid, which is, of course, that of the *unhydrolysed* salt. The concentration of the free urea, that is, of the *hydrolysed* salt, is therefore $c - (1 - k/k_0)$. Substituting in the general formula—

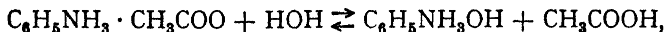
$$\frac{[\text{free base}]\,[\text{free acid}]}{[\text{unhydrol. salt}]} = \frac{[c - (1 - k/k_0)][k/k_0]}{1 - k/k_0} = K_h.$$

The values of the hydrolysis constant are given in the sixth column of the table, and are approximately constant, as the theory requires.

The degree of hydrolysis of a few salts of weak bases and strong acids in 1/10 molar solution at 25° is given in the table, and the results should be compared with the values for the dissociation constants of weak bases (p. 281) in order to illustrate equation (2).

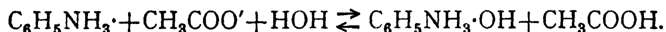
Salt.	Degree of hydrolysis.
Ammonium chloride . . .	0·005 per cent.
Aniline hydrochloride . . .	1·5 ,,
Thiazol hydrochloride . . .	19 ,,
Glycocoll hydrochloride . . .	20 ,,

Hydrolysis of the Salt of a Weak Base and a Weak Acid—The hydrolysis of aniline acetate, a typical salt of this class, is represented by the equation



$$C_6H_5NH_3 \cdot CH_3COO + HOH \rightleftarrows C_6H_5NH_3OH + CH_3COOH,$$

which, on the assumption that the salt is completely, the base and acid not at all, ionized, may be written as follows :—



$$C_6H_5NH_3^{\cdot} + CH_3COO' + HOH \rightleftarrows C_6H_5NH_3{\cdot}OH + CH_3COOH.$$

Applying the law of mass action, and using the former symbols,

$$\frac{[BOH][HA]}{[B^{\cdot}][A^{\cdot}]} = \frac{[\text{base}]\,[\text{acid}]}{[\text{unhydrol. salt}]^2} = K_h = \frac{K_w}{K_a K_b}.$$

If we express the *amounts* (in mols) of the base, acid and salt respectively in volume v of the solution by b, a, and s respectively, the above equation becomes

$$\frac{\left(\frac{a}{v}\right)\left(\frac{b}{v}\right)}{\left(\frac{s}{v}\right)^2} = \frac{ab}{s^2} = K_h,$$

that is, *the degree of hydrolysis of the salt of a weak base and a weak acid is independent of the dilution.* Experiment shows that in dilutions of 12·5 and 800 litres, aniline acetate is hydrolysed to the extent of 45·4 and 43·1 per cent. respectively; the slight deviation from the requirements of the theory is doubtless due to the fact that the assumptions made in deducing the above formula are only approximately true.

Determination of the Dissociation Constant for Water—It has been shown above that the process of hydrolysis in the case of a salt of a strong base and a weak acid may be looked upon as a distribution of the base between the weak acid and water acting as an acid, and the degree of hydrolysis therefore depends on the relative strengths of the weak acid and water. The relationship between these three factors is expressed by the equation

$$\frac{[\text{free acid}]\,[\text{free base}]}{[\text{unhydrol. salt}]} = K_h = \frac{K_w}{K_a}$$

where K_h is the hydrolysis constant, K_a the dissociation constant for the acid, and K_w the ionic product for water. It is clear that if the degree of hydrolysis of a salt and the dissociation constant of the acid are known, K_w can be calculated, and this is one of the most accurate methods for determining the degree of dissociation of water. As an illustration, we may calculate K_w from Shields's value for the hydrolysis of sodium acetate—0·008 per cent. in 0·1 molar solution at 25° (Arrhenius, Feb., 1893). We have

$$C_{acid} = C_{base} = 0{\cdot}00008 \times 0{\cdot}1,$$

$$C_{salt} = 0{\cdot}1 \text{ (the amount hydrolysed being negligible in comparison).}$$

Hence $$\frac{(0{\cdot}00008 \times 0{\cdot}1)^2}{0{\cdot}1} = 0{\cdot}64 \times 10^{-9} = K_h.$$

Now $K_w = K_h K_a = (0{\cdot}64 \times 10^{-9}) \times (1{\cdot}8 \times 10^{-5}) = 1{\cdot}16 \times 10^{-14}$.

Since $[H^{\cdot}][OH']$ is thus found to be approximately $1{\cdot}2 \times 10^{-14}$, the concentration of $H^{\cdot}$ or OH' ions (mols per litre) in water at 25° is $1{\cdot}1 \times 10^{-7}$.

K_w can also be calculated from measurements of the hydrolysis of salts of strong acids and weak bases, and, perhaps with still greater accuracy, from measurements with salts of weak acids and weak bases[1] by means of the formula

$$K_h = K_w / K_a K_b.$$

The degree of dissociation of water has been determined by three other methods at 25° with the following results :—

E.M.F of hydrogen-oxygen cell (Ostwald, January, 1893) (corrected value), $1{\cdot}0 \times 10^{-7}$ at 25°.
Velocity of hydrolysis of methyl acetate (van't Hoff-Wijs, March, 1893), $1{\cdot}2 \times 10^{-7}$ at 25°.
Conductivity of purest water (Kohlrausch, 1894), $1{\cdot}05 \times 10^{-7}$ at 25°.

When it is borne in mind how small the dissociation is, the close agreement in the values obtained by these four

[1] Lunden, *J. Chim. Phys.*, 1907, **5**, 574; Kanolt, *J. Amer. Chem. Soc.*, 1907, **29**, 1402.

independent methods is very striking, and forms a strong justification for the original assumption that water is split up to an extremely small extent into ions.

The question can be still further tested by applying van't Hoff's equation connecting heat development and displacement of equilibrium to the equilibrium between water and its ions. For the degree of dissociation at different temperatures, the following values were obtained by Kohlrausch from conductivity measurements :—

Temperature . .	0°	2°	10°	15°	26°	34°	42°	50°
Degree of dissociation	0·35	0·39	0·56	0·8	1·09	1·47	1·93	$2·48 \times 10^{-7}$

From any two of these measurements the heat development, Q, of the reaction, $H_2O \rightleftarrows H^{\cdot} + OH'$, can be calculated by substitution in the general formula (p. 173),

$$\log_{10} K_1 - \log_{10} K_2 = \frac{Q}{4·581}\left(\frac{T_2 - T_1}{T_2T_1}\right)$$

From the values[1] of K at 0° and 50°, Q = − 13,740 cal., and from that at 2° and 42°, Q = − 13,780 cal.

In a previous section (p. 289) it has been pointed out that, according to the electrolytic dissociation theory, the neutralization of a strong base by a strong acid consists essentially in the combination of $H^{\cdot}$ and OH' ions to form water. The heat given out in the reaction is about 13,700 cal. for molar quantities, in excellent agreement with the above value. This supports the assumption that the variation of the conductivity of pure water with temperature is due to the displacement of the equilibrium $H^{\cdot} + OH' \rightleftarrows H_2O$, in the direction indicated by the lower arrow. The value of Q, obtained directly as above, may be termed the *heat of ionization* of water; it is the heat given out when 1 mol of $H^{\cdot}$ and OH' ions combine to form water.

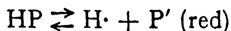
The heat of ionization of any electrolyte can naturally be calculated in the same way from the displacement of the equilibrium with temperature. The effect of increased temperature

[1] $K_2 = (2·48 \times 10^{-7})^2$ at 50°; $K_1 = (0·35 \times 10^{-7})^2$ at 0° (p. 288)

on the degree of ionization is almost always slight, and in the majority of cases the ionization is slightly diminished. As an illustration, the degree of electrolytic dissociation for 1/10 molar sodium chloride over a wide range of temperature, as determined by Noyes and Coolidge,[1] may be quoted. The values obtained were 84 per cent. at 18°, 79 per cent. at 140°, 74 per cent. at 218°, 67 per cent. at 281°, and 60 per cent. at 306°. Corresponding with the small variation in the degree of ionization with temperature, the heat of ionization is small, and may be positive (as in the present case) or negative.

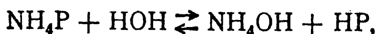
Theory of Indicators—The indicators used in acidimetry and alkalimetry have the property of giving different colours depending on whether the solution is acid or alkaline. According to Ostwald's theory, which has met with fairly general acceptance, such indicators, including methyl-orange, phenolphthalein and *p*-nitrophenol, are weak electrolytes, and their use depends on the fact that the ions and the non-ionized compounds have different colours. Since salts are almost always highly ionized, it is clear that only weak acids and bases can be employed as indicators.

Phenolphthalein is a very weak acid, the non-ionized acid is colourless, and the negative ion red. In aqueous solution it is ionized according to the equation



$$HP \rightleftarrows H^{\cdot} + P' \text{ (red)}$$

(where P′ is the negative ion), but so slightly that the solution is practically colourless. If now sodium hydroxide is added, the highly-dissociated sodium salt is formed, and the solution is deeply coloured owing to the presence of the red anion, P′. If, on the other hand, the solution contains a slight excess of acid, the increased H· ion concentration drives back the ionization of the phenolphthalein in the direction indicated by the lower arrow, and the solution becomes colourless (*cf.* p. 281). Finally, if a weak base, such as ammonium hydroxide, is added, the ammonium salt will be partly hydrolysed, according to the equation

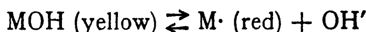


$$NH_4P + HOH \rightleftarrows NH_4OH + HP,$$

[1] *Zeitsch. Physikal. Chem.*, 1904, **46**, 323.

and excess of the base will be required in order to drive back the hydrolysis (p. 294); in other words, there will not be a sharp change of colour when ammonium hydroxide is added.

Methyl-orange has both acidic and basic properties. It was formerly regarded as an acid indicator, but it is now assumed to function as a very weak base. The undissociated substance is yellow and the cation is red. In aqueous solution it is ionized to some extent according to the equation



$$\text{MOH (yellow)} \rightleftarrows \text{M}^{\cdot} \text{ (red)} + \text{OH}'$$

so that the solution shows a mixed colour. On addition of alkali the equilibrium is displaced towards the left, the yellow undissociated substance being formed. As methyl-orange is a very weak base, this change is brought about by a small concentration of OH′ ions and therefore methyl orange is a suitable indicator for weak bases. When, on the other hand, an acid is added, the H· ions combine with the OH′ ions of the base to form water, the equilibrium is displaced towards the right, and, the resulting salt being largely ionized, the red colour of the cation appears. Owing to hydrolysis a considerable concentration of H· ions is required to bring about this change (compare phenolphthalein) and therefore methyl-orange is not a suitable indicator for weak acids.

The considerations to be borne in mind in selecting an indicator, or in choosing a suitable alkali for titrating an acid, or *vice versâ*, may be put concisely as follows (Abegg) :—

Solutions used.		Indicator.	Examples.
Acid.	Base.		
Strong	Strong	Any	Any.
Strong	Weak	Weak base or strong acid	Methyl-orange, *p*-nitrophenol.
Weak	Strong	Weak acid	Phenolphthalein, litmus.
Weak	Weak	None satisfactory	Should be avoided.

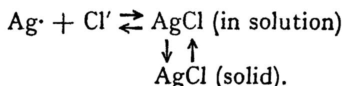
Some investigators maintain that the ionization theory does not give a satisfactory representation of the behaviour of indicators, but that the changes of colour are due to changes of

constitution, usually from the benzenoid to the quinonoid type and *vice versâ*.[1] In an aqueous solution of phenolphthalein, for instance, there are only traces of the quinonoid (coloured) modification, and the solution is colourless, but on the addition of alkali the phenolphthalein salt is formed, the negative ions of which, being of the quinonoid type, are strongly coloured.

The Solubility Product—We have now to consider an equilibrium of rather a different type—in which the solution is *saturated* with regard to the electrolyte. In such a case there is equilibrium between the solid salt and the *non-ionized* salt in the solution, so that the concentration of the non-ionized salt remains constant at constant temperature. Further, there is equilibrium in the solution between the non-ionized salt and its ions, which may be represented, in the case of silver chloride, for example, by the equation $Ag^{\cdot} + Cl' \rightleftarrows AgCl$. Applying the law of mass action, we have, for the latter equilibrium,

$$[Ag^{\cdot}][Cl'] = K[AgCl] = S,$$

where S is the product of the concentrations of the two ions —the so-called *solubility product*—and is constant, since the right-hand side of the above equation is constant. The equilibria in the heterogeneous system may be represented as follows :—



$$\begin{array}{c} Ag^{\cdot} + Cl' \rightleftarrows AgCl \text{ (in solution)} \\ \downarrow\uparrow \\ AgCl \text{ (solid).} \end{array}$$

As will be shown later, the solubility product for silver chloride at 25° is $1 \cdot 56 \times 10^{-10}$, when the ionic concentrations are expressed in mols per litre. If the solution has been prepared by dissolving the salt in water, the ions are necessarily present in equivalent proportions, so that a solution of silver chloride, saturated at 25°, contains $\sqrt{1 \cdot 56 \times 10^{-10}} = 1 \cdot 25 \times 10^{-5}$ mols of $Ag^{\cdot}$ and of Cl' ions.

The ions need not, however, be present in equivalent proportions; if by any means the solubility product is exceeded, for example, by adding a salt with an ion in common with the electrolyte, the ions unite to form undissociated salt, which falls

[1] *Cf.* Hewitt, *Analyst*, 1908, **33**, 85.

out of solution, and this goes on till the normal value of the solubility product is reached. Perhaps the best-known illustration of this is the precipitation of sodium chloride from its saturated solution by passing in gaseous hydrogen chloride. In this case the original equilibrium between equivalent amounts of Na· and Cl′ ions is disturbed by the addition of a large excess of Cl′ ions, and sodium chloride is precipitated till the original solubility product is regained, when the solution contains an excess of Cl′ ions and relatively few Na· ions.

As already mentioned, the difference between the present form of equilibrium and those previously considered is that the concentration of the non-ionized salt in the solution is constant at constant temperature. If it is diminished in any way, salt is dissolved till the original value is reached; if it is exceeded, as in the case just mentioned, salt falls out of solution till the original value is reached.

Since the equilibrium equation for a binary salt is symmetrical with regard to the two ions, it follows that the solubility of such a salt should be depressed to the same extent by the addition of equivalent amounts of its common ions, whether positive or negative. This consequence of the theory was tested by Noyes, who determined the influence of the addition of equivalent amounts of hydrochloric acid and of thallous nitrate on the solubility of thallous chloride, with the following results:—

Solubility of thallus chloride at 25°:—

Concentration of Substance added (mols per litre).	$TlNO_3$ added.	HCl added.
0	0·0161	0·0161
0·0283	0·0084	0·0083
0·147	0·0032	0·0033

The figures in the first column show the amounts of thallous nitrate and of hydrochloric acid added, those in the second and third columns represent the solubility of thallous chloride in mols per litre. The results show that the requirements of the theory are satisfactorily fulfilled.

The above results hold independently of the relative amounts of ions and non-ionized salt in the solution. Since in dilute solution all salts are highly ionized, it may, however, be assumed that difficultly soluble salts, such as silver chloride, are almost completely ionized in solution ; in other words, the concentration of non-ionized salt in solution may be regarded as negligible in comparison with that of the ions. This deduction is of great importance in estimating the solubility of difficultly soluble salts (see next page).

Applications to Analytical Chemistry—The above considerations with regard to the solubility product are of the greatest importance for analytical chemistry. A precipitate can only be formed when the product of the ionic concentrations attains the value of the solubility product, which for every salt has a definite value depending only on the temperature. For example, magnesium hydroxide is precipitated from solutions of magnesium salts by ammonia because the solubility product $[Mg^{\cdot\cdot}][OH']^2$ is exceeded. When, however, ammonium chloride is previously added in excess to the hydroxide, the OH' ion concentration is diminished to such an extent (p. 282) that the solubility product is not reached, and precipitation no longer occurs. Similarly, zinc sulphide is precipitated when the product $[Zn^{\cdot\cdot}][S'']$ exceeds a certain value. In alkaline solution, an extremely small concentration of hydrogen sulphide suffices for this purpose, as the sulphide is considerably ionized, but in acid solution the depression of the ionization of the hydrogen sulphide, in other words, the diminution in the concentration of S'' ions, is so great that the solubility product is not reached. On the other hand, the solubility product for certain heavy metals, such as lead, copper, and bismuth, is so small that it is reached even in acid solution. It is, however, possible to increase the acid concentration (and therefore to diminish the S'' ion concentration) to such an extent that the ionic product is not reached even for some of the above metals, for example, lead sulphide in concentrated hydrochloric acid is not precipitated by a current of hydrogen sulphide.

On the same basis, a fact which has long been familiar in quantitative analysis, that precipitation is more complete when excess of the precipitant is added, can readily be accounted for.

A saturated aqueous solution of silver chloride contains about $1\cdot25 \times 10^{-5}$ gram equivalents of the salt per litre, and the addition of ten times that concentration of Cl′ ions (added in the form of sodium chloride) will diminish the amount of silver in solution to about 1/10 of its original value (on the assumption that the concentration of the non-ionized salt is negligible in comparison with that of the ions) (*cf.* p. 282). It is thus evident that in the gravimetric estimation of combined chlorine as silver chloride there might be considerable error owing to the solubility of silver chloride in water, but if a fair excess of the precipitant is used, the error is quite negligible.

The concentration in saturated solution at 25°, and the solubility product of a few difficultly soluble salts are given in the accompanying table:—

Salt.	Saturation Concentration (mols per litre).	Solubility Product (mols per litre).
Silver chloride	$Ag^{\cdot} = 1\cdot25 \times 10^{-5}$	$1\cdot56 \times 10^{-10}$
,, bromide	,, $= 6\cdot6 \times 10^{-7}$	$4\cdot35 \times 10^{-13}$
,, iodide	,, $= 1\cdot0 \times 10^{-8}$	$1\cdot0 \times 10^{-16}$
Thallous chloride	$Tl^{\cdot} = 1\cdot6 \times 10^{-2}$	$2\cdot6 \times 10^{-4}$
Cuprous chloride	$Cu^{\cdot} = 1\cdot1 \times 10^{-3}$	$1\cdot2 \times 10^{-6}$
Lead sulphide	$Pb^{\cdot\cdot} = 5\cdot1 \times 10^{-8}$	$2\cdot6 \times 10^{-15}$
Copper sulphide	$Cu^{\cdot\cdot} = 1\cdot1 \times 10^{-21}$	$1\cdot2 \times 10^{-42}$

Experimental Determination of the Solubility of Difficultly Soluble Salts—When a saturated solution of a relatively insoluble salt is so dilute that complete ionization may be assumed ($\mu_v = \mu_\infty$), the solubility of the salt may readily be obtained from electrical conductivity measurements. The molecular conductivity at infinite dilution, μ_∞, can be obtained indirectly (p. 264), the specific conductivity of the saturated solution is determined in the usual way, and, by substitution in the formula $\mu_\infty = \kappa v$, we obtain the value of v, that is, the volume in c.c., in which a mol of the substance is dissolved. If the solubility is required in mols per litre, then

$$v = 1000\ \text{V, and}$$
$$\mu_\infty = 1000\ \kappa\text{V},$$

where V is the volume in litres in which a mol of the substance is dissolved. As the specific conductivity of such a

solution is small, the conductivity of the water becomes of importance, and it is necessary to subtract from the observed specific conductivity of the solution the conductivity of the water, determined directly. For such measurements, "conductivity" water, of a specific resistance not much less than 10^6 ohms, should be used.

As an example of the determination of solubilities by this method, Böttger found that a solution of silver chloride saturated at 20° had $\kappa = 1{\cdot}33 \times 10^{-6}$ after subtracting the specific conductivity of the water. Hence, as μ_∞ for silver chloride at 20°, determined indirectly (p. 264), is 125·5, we obtain, by substitution in the above formula,

$$125{\cdot}5 = 1000 \times 1{\cdot}33 \times 10^{-6}V,$$

$$\text{and} \quad V = \frac{125{\cdot}5}{1{\cdot}33 \times 10^{-3}} = 94{,}400,$$

that is, 94,400 litres of a solution of silver chloride, saturated at 20°, contain 1 mol of the salt. In one litre of solution there is, therefore, $1/94{,}400 = 1{\cdot}06 \times 10^{-5}$ mol, or 0·00152 gram of silver chloride. The values for the solubility of a number of difficultly soluble salts obtained by this method are given in the previous section (p. 306).

Complex Ions—Complex ions have already been defined as being formed by association of ions with non-ionized molecules. It is well known that though silver halogen salts are only slightly soluble in water they are readily soluble in the presence of ammonia. This phenomenon is due to the formation of complex ions (p. 287), in which the $Ag^{\cdot}$ ions are associated with ammonia molecules, forming univalent ions of the type $Ag(NH_3)^{\cdot}_x$. As nearly all the silver is present in this form and very little in the form of $Ag^{\cdot}$ ions, it is evident that a solution may contain a very considerable amount of a silver salt before the solubility product $[Ag^{\cdot}][X']$ is reached.

The composition of complex ions can be determined by a number of methods, including electrical migration measurements, distribution measurements, and solubility determinations. Thus the fact that the silver moves towards the anode when an electric current is passed through a solution of potassium silver cyanide shows that the metal in question is a

constituent of a complex anion, and from the alteration in the composition of the anode solution caused by the passage of a known quantity of electricity it can be shown that the anion has the formula $Ag(CN)_2'$. In certain cases (*e.g.*, solutions of cupric chloride and of cadmium iodide) the metal migrates, for the most part, to the cathode in dilute solution, and to the anode in concentrated solution. This observation is readily accounted for if complex ions are formed which undergo partial dissociation on dilution, *e.g.*—$CdI_2 + 2I' \rightleftarrows CdI_4''$.

Distribution measurements have been used to determine the composition of the azure blue solutions obtained by adding ammonia in excess to solutions of cupric salts. From a comparison of the partition of ammonia between chloroform and water alone and between chloroform and water containing varying amounts of a cupric salt it was shown that each atom of copper bound four molecules of ammonia, forming complex $Cu(NH_3)_4''$ ions. Similarly, from observations of the effect of potassium iodide (added to the aqueous layer) on the distribution of iodine between water and carbon disulphide the conclusion was formed that complex I_3' ions (together with the complex salt KI_3) are present in the aqueous solution.

Solubility measurements were made use of in determining the composition of ammoniacal solutions of **silver salts.** The amounts of silver chloride taken up by aqueous solutions of ammonia of various concentrations were determined, and, by application of the law of mass action, it was found that the expression $\frac{[Ag^{\cdot}][NH_3]^2}{Ag(NH_3)^{\cdot}_2}$ was most nearly constant, and, therefore, that the complex ion present in the solution in largest proportion is $Ag(NH_3)^{\cdot}_2$, corresponding with the complex salt $Ag(NH_3)_2Cl$. It is interesting to note that the only solid complex salt which has been separated from such solutions has the formula $2AgCl, 3NH_3$.

Influence of Substitution on Degree of Ionization—Reference has already been made to the influence of substitution on the strength of acids. As the effect of substitution on the degree of ionization has been most extensively investigated for this class of compound, a few further examples may be given. In the accompanying table, the affinity or dissociation constants

for some mono-substituted acetic acids are given, the value of K holding for 25° (concentrations in mols per litre).

Acetic acid $CH_3COO \cdot H$	0·000018
Propionic acid $CH_3CH_2COO \cdot H$ . . .	0·000013
Chloroacetic acid $CH_2ClCOO \cdot H$ . . .	0·00155
Bromoacetic acid $CH_2BrCOO \cdot H$ . . .	0·00138
Cyanacetic acid $CH_2CNCOO \cdot H$ . . .	0·00370
Glycollic acid $CH_2OHCOO \cdot H$ . . .	0·000152
Phenylacetic acid $C_6H_5CH_2COO \cdot H$ . .	0·000056
Amidoacetic acid $CH_2NH_2COO \cdot H$ . .	$3 \cdot 4 \times 10^{-10}$

As the carboxyl group only is concerned directly in ionization, the above table affords an excellent illustration of the influence of a group on a neighbouring one. The table shows that when one of the alkyl hydrogens in acetic acid is displaced by Cl, Br CN, or OH or C_6H_5 an increase in the activity of the acid is brought about; the effect is least for the phenol group and greatest for the cyanogen group. On the other hand, the methyl group (in propionic acid) diminishes the activity slightly, and the amido group diminishes it enormously.

These observations can readily be accounted for[1] on the assumption that the atoms or groups take their ion-forming character into combination. Thus the Cl, Br, CN and OH groups, which tend to form negative ions, increase the tendency of the groups into which they enter to form negative ions. The "negative favouring" character of the phenyl group is slight but distinct. On the other hand, the so-called basic groups, such as NH_2, lessen the tendency of the group into which they enter to form negative ions, as is very strikingly shown in the case of amidoacetic acid. The methyl group has also a slight diminishing effect on the tendency of a group to form negative ions.

The magnitude of the influence of a substituent on a particular group depends on its distance from that group. This is very well shown by the influence of the hydroxyl group on the affinity constant of propionic acid.

[1] A complete theory of the phenomena in question has been worked out by Flürscheim (*Trans. Chem. Soc.*, 1909, **95**, 718; *Proc.*, 1909, 193).

Propionic acid $CH_3CH_2COO{\cdot}H$ . . .	0·0000134
Lactic acid $CH_3CHOHCOO{\cdot}H$ . . .	0·000138
β-oxypropionic acid $CH_2OHCH_2COO{\cdot}H$.	0·0000311

When the OH group is in the α (neighbouring) position its effect on the dissociation constant is more than four times as great as when it is in the β position.

It seems plausible to suppose that a comparison of the influence of groups in the *ortho*, *meta*, and *para* positions on the carboxyl group of benzoic acid might throw some light on the question of the relative distances between the groups in the benzene nucleus. The dissociation constants of benzoic acid and the three chlor-substituted acids are as follows :—

Benzoic acid C_6H_5COOH	0·000060
o- Chlorobenzoic acid $C_6H_4ClCOOH$ . .	0·00132
m- ,, ,, ,, . .	0·000155
p- ,, ,, ,, . .	0·000093

It will be observed that the presence of the halogen in the *ortho* position greatly increases the strength of the acid, and it is a general rule that the influence of substituents is always greatest in this position. The effect of substituting groups in the *meta* and *para* positions is much smaller, and the order of the two is not always the same. As the table shows, *m*-chlorobenzoic acid is rather stronger than the *para* acid, but on the other hand *p*-nitrobenzoic acid is somewhat stronger than the *meta* acid.

Similar considerations apply to the influence of substituents on the strength of bases, but, as is to be expected, the effect of the various groups is exerted in the opposite direction to that on acids. Thus the displacement of a hydrogen atom in ammonium hydroxide by the methyl group gives a stronger base (methyl amine) but the entrance of a phenyl group gives a much weaker base (aniline) (*cf.* p. 281).

Reactivity of the Ions—It is a well-known fact in qualitative analysis that in the great majority of cases the positive component of a salt (*e.g.*, the metal) answers certain tests, quite independently of the nature of the acid with which it is combined, and in the same way acids have certain characteristic reactions, independent of the nature of the base present. These facts are

plausibly accounted for on the electrolytic dissociation theory by assuming that the positive and negative parts of the salts (the ions) exist to a great extent independently in solution, and that the well-known tests for acids and bases are really tests for the free ions. Thus silver nitrate is not a general test for chlorine in combination, but only for chlorine ions. It is well known that potassium chlorate gives no precipitate with silver nitrate, although it contains chlorine; this is readily accounted for on the electrolytic dissociation theory because the solution of the salt contains no Cl' ions, but only ClO_3' ions, which give their own characteristic reactions. These views appear still more plausible when cases are considered in which the usual tests fail, for example, mercuric cyanide does not give all the ordinary reactions for mercury. This could be accounted for by supposing that the compound is not appreciably ionized in solution, so that practically no $Hg^{\cdot\cdot}$ ions are present, and as a matter of fact the aqueous solution of mercuric cyanide is practically a non-conductor.

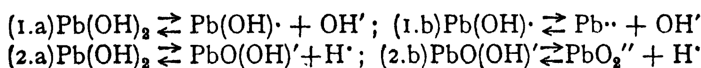
The chief characteristic of ionic reactions is their great rapidity; they are for all practical purposes instantaneous, and it is doubtful if the speed of a purely ionic reaction has so far been measured. It is well known that silver nitrate reacts with the chlorine in organic compounds such as ethyl chloride and chloracetic acid, but very slowly as compared with its action on sodium chloride. There is good reason for supposing that the reactions last mentioned are not ionic actions, but that the changes take place between the silver salt and combined chlorine.

The great reactivity of the ions in cases where it is known that they are actually present has led Euler and others to postulate that all reactions are ionic, and that in very slow reactions we are dealing with excessively small ionic concentrations.[1] This question cannot be adequately considered here, but it may be mentioned that the available experimental evidence does not seem to lend any support to Euler's theory. There is good reason to suppose that chemical reactions may take place between non-ionized molecules as well as between ions.

[1] Compare Arrhenius, *Electrochemistry* (English Edition), p. 180.

Amphoteric Electrolytes—It is a familiar fact that the hydroxides of certain polyvalent metals show both basic and acidic properties, since they form salts both with acids and bases, *e.g.*, lead hydroxide, $Pb(OH)_2$; aluminium hydroxide $Al(OH)_3$. In terms of the ionization theory, these compounds must give both hydrogen and hydroxyl ions on dissociation. Substances of this type, which can ionize in more than one way, are termed *amphoteric electrolytes.*

Lead hydroxide, $Pb(OH)_2$, can dissociate according to the following equations :—



(1.a) $Pb(OH)_2 \rightleftarrows Pb(OH)^{\cdot} + OH'$; (1.b) $Pb(OH)^{\cdot} \rightleftarrows Pb^{\cdot\cdot} + OH'$
(2.a) $Pb(OH)_2 \rightleftarrows PbO(OH)' + H^{\cdot}$; (2.b) $PbO(OH)' \rightleftarrows PbO_2'' + H^{\cdot}$

and doubtless all these compounds are present in greater or less concentration in an aqueous solution of lead hydroxide. It will of course be understood that the concentrations of $H^{\cdot}$ and of OH' ions cannot both be considerable in the same solution since the equilibrium $[H^{\cdot}][OH'] = K_{\omega}$ always holds (p. 289).

When an acid is added to the hydroxide, the OH' ions combine with the $H^{\cdot}$ ions of the acid to form water, more hydroxide dissociates according to equations 1a and 1b, the fresh OH' ions combine with the $H^{\cdot}$ ions to form water, and so on, till ultimately, if sufficient acid is added, the solution contains chiefly $Pb^{\cdot\cdot}$ ions and anions derived from the acid. If, on the other hand, alkali is added to the hydroxide, the OH' ions combine with the $H^{\cdot}$ ions derived from the hydroxide and dissociation proceeds progressively according to the upper arrows in equations 2a and 2b till ultimately the solution contains chiefly PbO_2'' ions and cations derived from the alkali added. The proof of the above statements is that on electrolysis the lead in acid solution travels to the cathode, in alkaline solution to the anode.

Some more complicated compounds can split off both $H^{\cdot}$ and OH' from a single molecule, leaving an uncharged ion or rather an ion which is both positively and negatively charged. For glycine (amidoacetic acid) we have the following equilibrium :—



$$OH\cdot H_3NCH_2COOH \rightleftarrows \overset{+}{H_3}NCH_2CO\overset{-}{O} + H^{\cdot} + OH'.$$

Ions of this type are termed *zwitter ions* or *hermaphrodite ions*. Since they are electrically neutral, they are not affected by an electric current.

Practical Illustrations—*Dilution Law. Conductivity of Acids and Salts*—Many of the results discussed in this chapter can be conveniently illustrated by means of the apparatus[1] shown in Fig. 39. The glass vessel each contains two circular electrodes of platinized platinum, the lower one is connected with

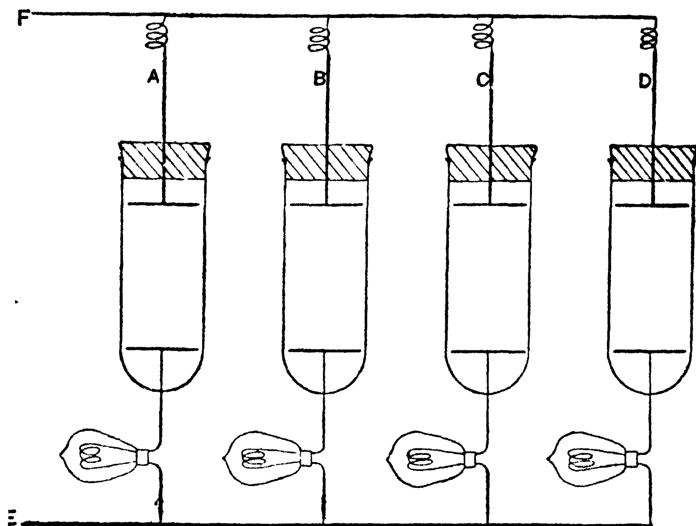


FIG. 39.

a wire which passes through the bottom of the vessel and is connected through a lamp to the wire E. The upper electrode, which is movable, is connected to a wire which passes through the cork loosely closing the vessel, and is connected to the upper wire F. The electrodes in each vessel should be of approximately the same cross-section, and the four lamps of equal resistance. The wires E and F are connected to the terminals of a source of alternating current, and as they are at constant

[1] Noyes and Blanchard, *J. Amer. Chem. Soc.*, 1900, **22**, 726.

potential throughout, the fall of potential through each of the vessels from E to F must be the same when a current is passing.

The use of the arrangement may be illustrated by employing it to prove the dilution law in the form $a = \sqrt{kv}$. Solutions of monochloracetic acid containing 1 mol of the salt in 1, 4, and 16 litres respectively are prepared, and the vessels A, B, and C nearly filled with them. When connection is made with the alternating current, it will be found that the brightness of the lamps is very different, but the positions of the upper electrodes can be so adjusted that the lamps are equally bright. Under these circumstances it is evident that the resistance of each solution is the same. On measuring the distances between the electrodes, it will be found that for the solutions $v = 1$, $v = 4$, $v = 16$, the distances are in the ratio 4 : 2 : 1. Hence, as the conductivities are inversely proportional to the distances between the electrodes, $a \propto \sqrt{v}$.

Further, it may be shown that, although acids differ very greatly in conductivity, neutral salts, even of weak acids, have a conductivity nearly as great as that of strong acids. The vessels are filled with 1/4 normal solutions of hydrochloric acid, sulphuric acid, monochloracetic acid and acetic acid respectively, and when the distances are altered till the lamps are equally bright, it will be found that the electrodes are very near in the acetic acid solution, far apart in the hydrochloric acid solution, and at intermediate distances for the other two acids. Sufficient sodium hydroxide to neutralize the acid is now added to each vessel, and after stirring and again adjusting to equal brightness of the lamps, it will be found that the distances for all four solutions are approximately equal.

Equilibrium Relations as shown by Indicators—The equilibrium relations in the case of weak acids and bases may be shown very well by means of indicators. Each of two beakers contains 100 c.c. of water, 1 c.c. of $n/1$ sodium hydroxide, and a few drops of methyl-orange. To the contents of one beaker n hydrochloric acid is added drop by drop by means of a pipette, and to the other n acetic acid is added in the same way till both solutions just become red. It will be observed that whereas about 1 c.c. of hydrochloric acid brings about the change of colour (owing to its relatively high con-

centration in H· ions), several c.c. of acetic acid are required to produce the same effect, owing to the much smaller H· ion concentration of the latter solution. If now a concentrated solution of sodium acetate is added to the last solution, the yellow colour of the methyl-orange will be restored; the acetate reduces the strength of the acid to such an extent (p. 282) that the H· ion concentration is no longer sufficient to drive back the hydrolysis of the methyl-orange salt.

The effect of hydrolysis may also be illustrated with indicators as follows: Each of two beakers contains 50 c.c. of 1/2 *n* hydrochloric acid and a few drops of methyl orange and phenolphthalein respectively. If *n* ammonium hydroxide is slowly added to the solution containing methyl-orange, the colour will change when about 25 c.c. of ammonia has been added, but a much greater quantity of the same solution will be required to redden the phenolphthalein solution. The explanation of this behaviour has already been given. Owing to the fact that the ammonium salt of phenolphthalein is considerably hydrolysed, it is necessary to add a fair excess of the base before the coloured phenolphthalein ions are produced in considerable amount.

The Solubility Product--The conception of the solubility product may be illustrated by the method employed by Nernst in proving the formula experimentally. A saturated solution of silver acetate is prepared by shaking the finely-powdered salt with water for some time. To a few c.c. of the solution in a test-tube a few c.c. of a fairly concentrated solution of silver nitrate are added, and to another portion of the acetate solution a solution of sodium acetate equivalent in strength to the silver nitrate solution, and the mixtures are well shaken. In each tube a precipitate of silver acetate will be formed.

Complex Ions—The evidence in favour of the view that in solutions of silver salts in potassium cyanide the silver is mainly present as a constituent of a complex anion, $Ag(CN)'_2$, is that the silver migrates towards the anode during electrolysis. The copper in Fehling's solution is also mainly present as a component of a complex anion, as may readily be shown qualitatively by a simple experiment described by Küster. A U-tube is about half-filled with a dilute solution of copper sulphate,

and the two limbs are then nearly filled up with a dilute solution of sodium sulphate in such a way that the boundaries remain sharp. A second U-tube is filled in an exactly similar way with Fehling's solution in the lower part and an alkaline solution of sodium tartrate in the upper part, the arrangement being such that the Fehling's solution in the one tube stands at the same level as the copper sulphate solution in the other tube. The U-tubes are then connected by a bent glass tube, filled with sodium sulphate solution, and with the ends dipping in the sulphate and tartrate solutions respectively. A small current is then sent through the U-tubes in series, by means of poles dipping in the outer limbs of the tubes, and after a time it will be observed that the copper sulphate boundary has moved with the positive current, whilst the coloured boundary in the other tube has moved against the positive current towards the anode. It is therefore evident that in the latter case the copper is present in the anion, as stated above.

Chemical Activity and Ionization—The great difference in chemical and electrical activity produced by ionization is well shown by comparing the properties of solutions of hydrochloric acid gas in water and in an organic solvent such as toluene. Whilst the former solution conducts the electric current and dissolves calcium carbonate rapidly, the latter solution is a non-conductor, and has little or no effect on calcium carbonate.

The same fact is illustrated by the interaction of silver nitrate with potassium bromide, ethyl bromide and phenyl bromide respectively in alcoholic solution. Approximately 5 per cent. solutions of the bromides in ethyl alcohol are prepared, and to each solution is added a few c.c. of a saturated solution of silver nitrate in alcohol. With the potassium bromide there is an immediate precipitate, the action being ionic. With ethyl bromide the reaction is very slow, and there is no apparent reaction with phenyl bromide. The reaction between silver nitrate and ethyl bromide is a good example of a chemical change which is not ionic, as far as one of the reacting substances (the ethyl bromide) is concerned.

Non-ionic chemical changes may, however, be very rapid. A solution of copper oleate in perfectly dry benzene reacts immediately with a solution of hydrochloric acid gas in dry benzene, with precipitation of cupric chloride (Kahlenberg).

CHAPTER XII

COLLOIDAL SOLUTIONS.[1] ADSORPTION

Colloidal Solutions. General—Up to the present we have dealt with substances which on the basis of their osmotic and electrical behaviour may be classed either as electrolytes or non-electrolytes. In the present chapter we are concerned with a new type of substance which differs in many respects both from typical electrolytes and non-electrolytes. The first discoveries in this field we owe to Thomas Graham (1861) who found that whilst certain substances diffuse rapidly in solution and readily pass through animal and vegetable membranes, other substances diffuse very slowly in solution and are unable to pass through membranes. To the first class of substances, which can readily be obtained in crystalline form, Graham gave the name *crystalloids*, whilst the members of the other class, which cannot as a rule be obtained in crystalline form, were termed *colloids*. Most inorganic acids, bases, and salts and many organic compounds, such as acetic acid, cane sugar, and urea are crystalloids; starch, gum, gelatine, caramel, and proteins in general belong to the group of colloids. The differences in the rates of diffusion in aqueous solution of typical crystalloids and colloids are illustrated in the following numbers,

	Crystalloids.			Colloids.	
Substance . .	HCl	NaCl	Cane Sugar	Albumen	Caramel
Relative times of equal diffusion	1	2·3	7	49	98

[1] For fuller details of the subjects treated of in this chapter see Philip, *Physical Chemistry: Its Bearing on Biology and Medicine* (Arnold, 1910); Freundlich, *Kapillarchemie* (Leipzig, 1922); Wolfgang Ostwald, *Kolloidchemie* (Dresden, 1911).

valid for 10°, which represent the relative times required for the same amount of diffusion of different substances.

As under equivalent conditions the rate of diffusion is proportional to the osmotic pressure of the solute, it follows that the osmotic pressure of dissolved colloids is very small and therefore that their molecular weights are very high. This view as to the high molecular weight of colloids was held by Graham, who suggested that the differences in behaviour of the two classes of substances might be connected with the much greater size of colloidal particles as compared with dissolved particles of crystalloids. It may be said at once that later investigation has fully confirmed the view as to the high molecular weight of colloids in solution.

As was to be anticipated, the later developments of the subject have led to modifications of Graham's views in some essential respects. In the first place it has been shown that colloids are not a special class of substances; *the colloidal state is a condition into which practically all chemical substances can be brought by suitable methods.* For example, metals such as silver and platinum, and even salts such as silver chloride and sodium chloride, all of which are ordinarily met with in crystalline form, can be obtained in colloidal solution. There are, however, great differences in the readiness with which different substances can be brought into the colloidal state, and some substances, such as starch and gelatine, are only met with in solution in the colloidal form.

A further point, which has been established within the last few years, is that colloidal solutions are not solutions in the ordinary sense of the term. A true solution has been defined as a *homogeneous* mixture, and therefore consists of a single phase. A colloidal solution, on the other hand, such as colloidal platinum, can be shown to be *heterogeneous*; that is, it consists of two phases at least. As we shall see later, however, all intermediate stages exist between colloidal solutions and true solutions on the one hand, and between colloidal solutions and ordinary suspensions on the other. Within the last few years it has become usual to speak of the phase present in separate particles as the *disperse* phase and the liquid in which it is distributed as the *dispersion medium.*

The preparation of some typical colloidal solutions, and the properties characteristic of the colloidal state, will now be considered.

Preparation of Colloidal Solutions—A suitable colloidal solution for demonstration purposes is that of arsenious sulphide. It is prepared by passing hydrogen sulphide through a cold aqueous solution of arsenious oxide, free from electrolytes, sufficiently long to ensure conversion to arsenious sulphide. Excess of hydrogen sulphide is then removed as far as possible by a stream of hydrogen. The resulting solution, after filtration, is yellowish in colour and clear by transmitted light, but appears turbid by reflected light. The degree of dispersion of the sulphide (that is, the size of the particles) varies greatly with the mode of preparing the solution.

Silicic acid is obtained in colloidal solution by slowly adding a solution of sodium silicate to excess of hydrochloric acid and then removing the sodium chloride and free hydrochloric acid by dialysis. The simplest form of dialyser is a tube of parchment paper into which the mixture is poured. The tube is then suspended by its ends in water which is continually renewed, and in course of time the crystalloids are completely removed by diffusion through the membrane, leaving a pure colloidal solution of silicic acid.

Ferric hydroxide is obtained in colloidal solution (so called "dialysed iron") by dissolving the freshly precipitated hydroxide in a dilute solution of ferric chloride, and removing the ferric chloride by dialysis. Other colloidal hydroxides may be obtained by an analogous method.

The preparation of colloidal platinum according to Bredig has already been described (p. 239). Other colloidal metals (*e.g.*, gold, silver, palladium) have been prepared by the same method. Colloidal gold and other metals can also be prepared by reducing the corresponding salts in aqueous solution.

Gelatine, gum, and certain other substances form colloidal systems on simple solution in water.

Osmotic Pressure and Molecular Weight of Colloids—It has already been mentioned that, corresponding with their slow rate of diffusion, the osmotic pressure of colloidal solutions is very small. This is fully confirmed by recent investigations,

but direct quantitative measurements by different observers have not led to very concordant results. One of the principal sources of error has been the difficulty of freeing colloids completely from electrolytes, which even in very small concentration have considerable osmotic pressure. This difficulty is to some extent overcome by using another colloid, such as parchment paper, as semi-permeable membrane; one colloid, whilst usually permeable for crystalloids, is impermeable to other colloids. Hence, as parchment paper and other membranes are permeable for dissolved salts, the latter cannot set up a *lasting* osmotic pressure, and a pressure which persists for a considerable time may be regarded as due to the colloid only.

As illustrating the nature of the results obtained, Lillie,[1] using a collodion membrane, found that a solution of egg albumen containing 12·5 grams per litre gave an osmotic pressure of 20 mm. of mercury at room temperature. According to Waymouth Reid the osmotic pressure of a 1 per cent. solution of hæmoglobin is about 4 mm. of mercury, but much higher values, indicating a molecular weight of about 16,000, were obtained by Roaf (1910).

Moore and Roaf [2] observed a pressure of about 70 mm. of mercury for a 10 per cent. solution of gelatine, which remained fairly steady for two months.

The effect of electrolytes on the magnitude of the osmotic pressure depends on the nature of the colloid. Neutral salts in many cases lower the osmotic pressure of colloids, a result probably due to partial coagulation of the colloidal particles. Acids and bases often raise the osmotic pressure of colloids, probably in consequence of chemical combination.

As the osmotic pressure of colloids is so small when measured by the direct method it will readily be understood that the freezing-points and boiling-points of colloidal solutions scarcely differ from those of pure water. This is evident when we consider that a solution of osmotic pressure 70 mms. (as observed in the experiments just described) would have a freezing-point less than $\frac{1}{100}°$ below that of water.

[1] *Amer. Journal of Physiology*, 1907, **20**, 127.
[2] Moore and Roaf, *Biochem. Journ.*, 1906, **2**, 34.

Optical Properties of Colloidal Solutions—The majority of colloidal solutions appear homogeneous even under the highest power of the microscope, but their heterogeneous character is established by means of the so-called " Tyndall phenomenon." When a ray of light enters a darkened room its path is recognized by the scattering of the light at the surface of dust particles. Similarly, the path of a beam passed through a colloidal solution can be detected by the scattering of the light at the surface of the ultramicroscopic particles, whereas no indication is afforded of the path of a beam passed through a solution which contains no particles exceeding a certain magnitude. Light which has passed through a colloidal solution is partially or completely polarized.

The Tyndall phenomenon has recently been utilized in the construction of the ultramicroscope, by means of which our knowledge of colloidal solutions has been greatly extended. An intense beam of light (the arc light or, better, sunlight) is directed on a very thin layer of the colloid and the latter examined by a microscope at right angles to the direction of the beam, the entrance of light from other sources being prevented. When a homogeneous liquid is used the field remains quite dark, but when the liquid contains discrete particles their presence is indicated by the appearance of colourless or (for smaller particles) characteristically coloured luminous moving points on a dark background. It must be emphasized that the ultramicroscope does not render the particles themselves visible, but only shows the light reflected from them, so that such observations afford no information as to the shape, colour, etc., of the particles.

The average size of the particles in a colloidal solution can be estimated indirectly by counting the number in a given volume and determining the total amount of substance by analysis. In this way it has been shown that the particles vary greatly in magnitude, depending on the nature and mode of preparation of the colloidal solution, from such as are visible in the ordinary microscope to those not resolvable even by the ultramicroscope. Particles visible in the ordinary microscope (diameter exceeding 250 $\mu\mu$, where $\mu = 0{\cdot}001$ mm. and $\mu\mu = 0{\cdot}000001$ mm.) are termed by Zsigmondy *microns*, those detected

only by the ultramicroscope (diameter 6-250 $\mu\mu$) are termed *submicrons*, and those of diameter less than 6 $\mu\mu$ *amicrons*.

For comparative purposes it may be mentioned that the wave-length of sodium light is 589 $\mu\mu$. It has been calculated[1] that the diameter of an ether molecule is about $0{\cdot}6 \times 10^{-6}$ mm. $= 0{\cdot}6\ \mu\mu$, so that the smallest particle which can be detected by the ultramicroscope has a diameter only ten times greater than that of an average chemical molecule.

Brownian Movement—When a colloidal solution containing microns (*e.g.*, mercuric sulphide, suspension of gum mastic) is examined under the microscope, the particles are seen to be performing continuous irregular movements (R. Brown, 1827). " They go and come, stop, start again, *mount*, descend, *remount again*, without in the least tending towards immobility " (Perrin). Observations with the ultramicroscope show that the movements are the more brisk the smaller the particles and the less the viscosity of the liquid, and they become more rapid with rise of temperature. The phenomenon persists for years; it is not due to any external cause, such as alterations of temperature or of illumination, and it is now generally agreed that it is a consequence of " the incessant movements of the molecules of the liquid which, striking unceasingly the observed particles, drive them about irregularly through the fluid, except in the case where these impacts exactly counterbalance one another " (Perrin, *loc. cit.*). It has been shown within the last few years, more particularly by Perrin, that the rates of movement of the particles are in entire accord with those deducted on the basis of the molecular-kinetic theory, which amounts to an experimental proof of the atomic constitution of matter and of the kinetic nature of heat (*cf.* p. 38).

Electrical Properties of Colloids—When two plates are placed at some distance apart in a colloidal solution and connected with a source of E.M.F. it will be found as a rule that the particles move slowly towards the anode or cathode; in other words, they behave as if they are electrically charged. The simplest method of making the experiment is to place the colloidal solution in the lower part of a U-tube, which is filled

[1] Perrin, *Les Atomes*, 1921 (Eng. Trans., 1923), p. 50.

up on both sides with distilled water in which the electrodes are placed. The latter are then connected with the terminals of the lighting circuit (100-200 volts) and the speed of the moving boundary observed directly. The results show that particles of all kinds move at the rate of $10 \cdot 40 \times 10^{-5}$ cm. per second for a potential gradient of 1 volt per cm. As we have seen, this is also the order of the migration velocity of the ions (p. 259) and we have therefore the remarkable fact that particles of all sizes—microns, submicrons, amicrons, ions—move with approximately the same speed in the electric field.

In the case of the noble metals (gold, platinum, silver, etc.) and the sulphides (arsenic and antimony trisulphides) the particles are negatively charged and move towards the anode, whilst hydroxides (ferric and aluminium hydroxides, etc.) and hæmoglobin are positively charged. The charge on some colloids can, however, be altered in sign by certain additions to the medium. Thus Hardy has shown that when acid is added to egg albumen it migrates to the cathode, whilst in alkaline solution it moves towards the anode. The condition in which the colloid is uncharged is known as the *isoelectric point*, which in the case of egg albumen occurs in approximately neutral solution.

Precipitation of Colloids by Electrolytes—It is a remarkable fact that many colloidal solutions are readily coagulated by the addition of electrolytes. When, for example, a few drops of barium chloride solution are added to a colloidal solution of arsenic sulphide the solution becomes turbid, and in a few minutes the sulphide has completely separated in flocks. The process can be followed under the ultramicroscope, and is seen to consist in a gradual aggregation of the particles (amicrons to submicrons, then to microns and finally to large flocks) the Brownian movement becoming slower and slower and finally ceasing.

The efficiency of different electrolytes in the coagulation of arsenic sulphide depends mainly on the valency of the anion and is largely independent of its nature. The *molar* concentrations of $AlCl_3$, $BaCl_2$, and KCl required to produce same degree of coagulation under conditions otherwise equivalent are as follows: 1 : 7·4 : 532 (Freundlich). With solutions of ferric hydroxide, on the other hand, the coagulating power of

electrolytes is practically independent of the valency of the cation, and is determined chiefly by the valency of the anion. Thus the molar concentrations of K_2SO_4 and KCl which produced the same effect are in the ratio 1 : 45.

When it is remembered that the particles of arsenious sulphide are negatively charged and those of ferric hydroxide positively charged the bearing of these results at once becomes evident. *The ion which brings about the coagulation of a colloidal solution is the one carrying a charge of opposite sign to that on the colloidal particles* (Hardy). Further investigation has shown that this rule can be extended to the reciprocal action of colloidal particles, inasmuch as two colloidal solutions containing particles of contrary sign coagulate on mixing (*e.g.*, colloidal platinum and ferric hydroxide) whilst colloids of the same sign are practically without influence on each other.

As regards the nature of the coagulation, it has been shown that in certain cases at least the electrolyte is partially decomposed, the precipitating ion being carried down along with the precipitate and the inactive ion left in solution in combination with another ion. In order to understand this phenomenon it is necessary to consider rather more fully the question of the stability of a colloidal solution. It has been shown by Hardy, Burton, and others that certain colloids reach their point of maximum instability (that is, coagulate most readily) when the charge on the particles (as indicated by their behaviour under the influence of a potential gradient) reaches a minimum. Taking as illustration the coagulation of arsenious sulphide by potassium chloride solution we may assume that some of the salt is taken up by the colloidal particles, the negative charges on the latter are neutralized by the K· ions, with the result that the particles become unstable, aggregate and fall out of solution carrying the K· ions along with them (presumably as a salt). The Cl· ions are left in the solution along with an equivalent of H· ions derived from the hydrogen sulphide always associated with the colloidal sulphide. This is the so-called "adsorption" theory of coagulation. Other theories of the phenomenon, notably Billiter's "condensation" theory, have also been proposed, but cannot be dealt with here.[1]

[1] Wo. Ostwald, *Kolloidchemie*, p. 499.

Suspensions, Suspensoids, and Emulsoids—All the properties discussed in the previous sections (with the possible exception of the action of electrolytes on the stability) are characteristic of colloidal solutions in general, as well as of suspensions of particles easily visible under the microscope. As typical "suspensions" may be mentioned clay, finely divided charcoal or gum mastic stirred up with water. They consist of a practically insoluble solid phase, distributed in a liquid, usually water. The particles settle to the bottom of the vessel more or less rapidly, depending on their magnitude, but the system "clears" much more rapidly when electrolytes are added (*cf.* previous section). From the suspensions we pass through a series of intermediate stages to the suspensoids or suspension colloids, the heterogeneous character of which is only recognized by Tyndall's phenomenon or by the ultramicroscope. Like the suspensions, they consist of a solid phase distributed in a liquid, generally water. "Colloidal solutions" are divided into two fairly well-defined classes, the suspension colloids or suspensoids just mentioned and the emulsion colloids or emulsoids. The suspensoids are scarcely more viscous than water, do not gelatinize and are readily precipitated by electrolytes. The emulsoids are viscous, become gelatinous under certain conditions, and are not readily precipitated by electrolytes. The colloidal metals, sulphides, and hydroxides are suspensoids; silicic acid, gelatine, gum, mucilage of starch, and proteins in general are emulsoids. Emulsoids, like suspensoids, are two-phase systems, but consist of two liquid phases, one a honeycomb-like structure, rich in colloid, in the meshes of which the other phase, composed of a dilute solution of the colloid, is distributed. Thus an aqueous solution of gelatine is made up of two phases, one rich in water and containing a little gelatine in true solution, the other rich in gelatine, but containing a little water (Hardy).

It is a familiar fact that an emulsoid such as silicic acid can be obtained as a clear, apparently homogeneous solution (p. 319) which on long standing, more rapidly on boiling or on treatment with electrolytes, changes to a semi-solid amorphous mass. The clear solution is termed a *sol*, the gelatinous mass a *gel*. The term sol is also applied to suspensoids. When the

electrolyte is removed by washing and the gel is again treated with water certain emulsoids, such as the proteins, return to the sol modification (more readily on warming) and are therefore termed *reversible* colloids. Suspensoids in general and certain emulsoids, such as silicic acid, do not return to the soluble form under these conditions and are therefore known as *irreversible* colloids.

The coagulation of emulsoids by electrolytes seems to be entirely different to the action on suspensoids, but is by no means well understood. Whether the electrical character of the particles and of the electrolyte plays any part in the process is doubtful; in fact silicic acid sol seems to be most stable in the electrically neutral condition. The addition of neutral salts in considerable concentration causes the separation of the solid phase, but the ratio of the activities of different electrolytes is quite different from that observed for suspension colloids and resembles the "salting out" observed, for instance, in the effect on the solubility of gases in water (p. 96).

Filtration of Colloidal Solutions—It has already been pointed out that systems of all degrees of dispersion are met with, from those containing large particles easily visible under the microscope to molecular dispersed systems, which we term true solutions. It is evident, however, that true solutions are only apparently homogeneous; the solute particles are so minute as to escape our present methods of detecting heterogeneity. As already explained, the size of colloidal particles can be roughly estimated by counting the number in a given volume of solution containing a known weight of the disperse phase. Another method which has recently come into use for this purpose is to use filters with pores of different sizes. Bechhold,[1] who has done much work on this subject, uses filter-papers impregnated with gelatine solutions of different concentrations, and finds that a filter with 2 per cent. of gelatine retains all particles of diameter greater than 44 $\mu\mu$, one containing 4-4·5 per cent. is required to retain the much smaller particles of serum-albumen, the average molecular weight of which is about 10,000 (3,000-15,000). The permeability of such filters is of course influenced by the pressure under which filtration is carried

[1] *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 3.

out. A very early form of the "ultra-filter," introduced by Martin, consists of an ordinary porcelain filter impregnated with gelatine.

Adsorption. General—It is a familiar fact that when water containing a colcuring matter such as caramel or litmus is shaken up with finely divided charcoal the latter on settling carries down the colouring matter with it, leaving the water practically colourless. Further investigation shows that other substances, including electrolytes and non-electrolytes as well as colloids, are largely taken up by charcoal from aqueous solution, and that other finely divided substances have the same property. Charcoal has also the power of taking up gases, especially those which are easily liquefied, such as ammonia and sulphur dioxide.

The nature of this phenomenon will be more readily understood in the light of some quantitative observations, and for this purpose the results of a series of experiments carried out by Schmidt[2] on the taking up of acetic acid from aqueous solution by charcoal are quoted. Animal charcoal (in quantities of 5 grams) was shaken up with aqueous solutions of acetic acid (100 c.cs. in each case) of different concentrations and the amount of acid remaining in the water phase determined by titration. In the accompanying table A_c represents the amount of acetic acid taken up by the charcoal and A_w the amount left in solution at equilibrium.

DISTRIBUTION OF ACETIC ACID BETWEEN WATER AND CHARCOAL

A_c . .	0·93	1·15	1·248	1·43	1·62
A_w . .	0·0365	0·084	0·13	0·206	0·350
C_c^4/C_w .	205	208	180	203	197

As the volume of the solution and the amount of charcoal are kept constant, the amounts given in the table are proportional to the respective concentrations, C_c and C_w, in the two phases. The figures show (1) that in very dilute solution the acid is almost completely taken up by charcoal; (2) that the

[2] *Zeitsch. physikal. Chem.*, 1910, **74**, 689.

concentration in the charcoal increases much less rapidly than the concentration in the aqueous phase. That we are dealing with true equilibria is shown by the fact that the same results are obtained from either side (starting from concentrated or from dilute solutions of the acid).

The question now arises as to how these observations are to be interpreted. In the first instance we will consider whether the process is a physical or a chemical one, and if the former, whether it is mainly a surface condensation or whether solid solutions are formed.

It appears highly improbable for several reasons that the phenomena are chemical in nature. In the first place the most various substances, including argon and the other inactive gases, which do not, as far as is known, enter into chemical combination, are taken up by charcoal. Further, a definite chemical compound is constant in composition and, if undissociated, its composition is independent of the concentration in the other phase, whereas, as the table shows, the composition of the carbon-acetic acid system varies continuously within wide limits. At first sight it would appear possible to explain the results as being due to the formation of a partially dissociated solid compound in equilibrium with its products of dissociation, but it can easily be shown that this assumption also is incompatible with the facts. Applying the law of mass action to such an equilibrium (*in the liquid phase*) we have (*cf.* p. 184)

$$[\text{Absorbent}]^{n_1}\,[\text{Substance taken up}]^{n_2}/[\text{Compound}]^{n_3} = \text{Const.}$$

where the square brackets represent concentrations, and n_1, n_2, and n_3 represent the number of molecules of the absorbent (charcoal), the substance taken up (acetic acid) and the compound respectively taking part in the equilibrium. Further, since the active masses of the charcoal and the compound are constant—

$$[\text{Substance taken up}] = \text{Constant (in liquid phase)}$$

that is, the concentration of the acetic acid in the solution must be constant as long as both solid phases are present. As a matter of fact, the concentration of acetic acid in the solution increases *continuously* with the total concentration

(compare table), so that no second solid phase (no chemical compound) can be present.

The formation of a solid dissociating compound from a solid phase and a substance in solution has been investigated by Walker and Appleyard in the case of diphenylamine and picric acid, which combine to form the slightly soluble brown compound diphenylamine picrate.[1] Until the concentration of the acid in the aqueous layer reached 0·06 mol per litre the solid diphenylamine (which is practically insoluble in water) remained colourless, on further addition of picric acid the brown diphenylamine picrate began to form, and finally practically all the diphenylamine was converted into picrate, the concentration of the picric acid in the solution remaining all the time practically constant at 0·06 mol per litre. It is evident that the system exactly corresponds with the calcium carbonate—calcium oxide—carbon dioxide equilibrium already considered (p. 184), except that in the latter case the substance of variable concentration (the carbon dioxide) is in a gaseous and not in a liquid phase.

It remains to consider whether the phenomena in question, such as the taking up of acetic acid by charcoal, are due to surface condensation or whether solid solutions are formed. It would seem possible to decide this question at once by observing the rate of establishment of equilibrium, since surface condensation must be a very rapid process, and the formation of a solid solution, whereby (in the case under consideration) one substance has to diffuse into the interior of the other, must be very slow. As a matter of fact the establishment of equilibrium in many cases (but not in all cases, see below) is practically instantaneous, which lends strong support to the surface condensation theory. The strongest evidence in favour of the latter theory, however, is based on a consideration of the ratio of the distribution of the substance between the two phases. It has been shown (p. 188) that when a substance distributes itself between two phases the ratio of the distribution is independent of the concentration provided the molecular weight of the solute is the same in both solvents, but if the molecular weight in the solvent A is z times that in the

[1] **Walker and Appleyard, 1896, 69, 1334.**

solvent B then $\sqrt[z]{C_A}/C_B$ is constant, which may be written more conveniently thus: $C_A^{1/z}/C_B$ = Constant. Now the table on page 327 shows that for the distribution of acetic acid between water and charcoal the formula holds approximately

$$C_c^4/C_w = \text{Constant},$$

where C_c and C_w represent the concentrations in charcoal and in water respectively. Comparing this with the distribution formula $C_A^{1/z}/C_B$ = Constant, we find that

$$1/z = 4 \quad \text{or} \quad z = 1/4;$$

that is, if charcoal and water may be regarded as two solvents between which the acetic acid is distributed then the molecular weight of the acid in charcoal is 1/4 *that in water.* Now it was shown by Raoult that acetic acid exists as single molecules in aqueous solution, so that its molecular weight in charcoal, deduced on the assumption that it is present in solid solution, is an impossible one. Analogous results are obtained with other solutes and other absorbing agents, and it follows at once that the "solid solution" explanation of the phenomena under consideration is definitely disproved. There is evidence, however, that in some cases solid solution may play a subsidiary part in the phenomena. Thus Davis [1] found that when iodine is shaken up with charcoal a very rapid action is followed by a slow action, the latter being presumably due to the slow diffusion of the iodine into the interior of the charcoal. Similarly McBain [2] has shown that when hydrogen which has been n contact with charcoal for a long time is pumped out the greater part of it (that condensed on the surface) can be drawn off immediately, but a small residue (presumably present in solid solution) can only be removed very slowly.

It has now been established that the phenomenon under consideration is physical in nature and mainly at least due to surface condensation. In order to distinguish it from such a process as the absorption of gases in liquids, an example of true solution, the process is termed *Adsorption*, and the sub-

[1] *Trans. Chem. Soc.*, 1907, **91**, 1666.
[2] *Phil. Mag.*, 1909, **18**, 816.

stance which is condensed on the surface of the solid phase is said to be *adsorbed*.

Adsorption of Gases. Adsorption Formulæ—So far we have been concerned mainly with the adsorption of substances from solution. It is now necessary to deal a little more in detail with the fact already mentioned, that porous substances have a considerable adsorptive power for gases, and that those gases which are most easily liquefied are most largely adsorbed. The nature of the results is well shown by the accurate measurements of Homfray [1] and of Titoff [2] on the adsorption of gases by charcoal. The amount of gas adsorbed is proportional to the adsorbing surface and is the greater the lower the temperature and the higher the pressure. Titoff found that the adsorption of hydrogen follows Henry's law, so that the formula

$$C_A/C_B = \text{Constant}$$

applies, where C_A represents the concentration in the solid phase, C_B that in the gas phase. The other gases at low temperatures do not follow Henry's law, but the results are represented fairly satisfactorily by a formula of the type $C_A^{1/z}/C_B =$ Constant. The adsorptive power of charcoal for traces of gas, especially at low temperatures, has been used by Dewar to obtain the highest vacua yet reached; the pressures were too low to be capable of measurement.

It has been shown above that a formula of the type $C_A^{1/z}/C_B =$ Constant—an exponential formula—affords a fairly satisfactory representation of the adsorption both of gases and dissolved substances. In the literature it is met with in a slightly different form, which will now be given. Instead of writing $C_A^{1/z}/C_B$ we may put $C_A/C_B^z =$ Constant. When for C_A we put x/m, where x represents the amount of substance adsorbed by m grams of adsorbent, we obtain, putting p for C_B and $1/n$ for z, the formula

$$x/m = \beta p^{1/n},$$

where β and n are constant at constant temperature. When $1/n = 1$ the adsorption follows Henry's law, but in almost

[1] *Proc. Roy. Soc.*, 1910, **84**, A, 99.
[2] *Zeitsch. physikal. Chem.*, 1910, **74**, 641.

every instance $1/n$ is considerably less than 1. This expresses the important fact that adsorption is relatively greatest from dilute solution and falls off rapidly with the concentration (p. 327).

The Cause of Adsorption—Adsorption of gases and liquids occurs more or less at all solid surfaces, a well-known case in point being the adsorption of moisture by glass surfaces, but it is only when the surface is very large in comparison with the weight of the solid—as in the case of porous and finely divided substances—that it can readily be measured. We have now to consider why the concentration in the surface layers differs in many cases so greatly from that in the main bulk of the liquid or gas phase. It seems probable at the outset that this must be connected with molecular attraction at the boundary of the phases, in other words with the surface tension (p. 89), and the connection between surface tension and adsorption has been deduced theoretically by Willard Gibbs and by J. J. Thomson. From the general standpoint we must assume that not only increased concentration, but in certain systems a lowering of concentration at the surface, as compared with that in the main bulk of liquid, may occur. Calling an increase of concentration positive adsorption and a diminution negative adsorption, the rule may be expressed as follows: [1] *A dissolved substance is positively adsorbed when it lowers the surface tension, negatively adsorbed when it raises the surface tension.* The first case is met with in most solutions of organic compounds; the second in solutions of highly ionized inorganic salts.

Further Illustrations of Adsorption—One very important process in which adsorption plays a prominent part is the dyeing of fibres such as wool and silk. Whether dyeing is purely an adsorption phenomenon or whether chemical action also plays a part has given rise to a great deal of discussion, and is by no means finally settled. It has recently been shown that the distribution of crystal violet, new magenta, and patent blue between wool, silk, and cotton on the one hand, and water on the other is satisfactorily represented by the adsorption formula, and the value of the exponent $^1/_n$ is approximately the same as when charcoal is used as absorbent, a result which

[1] *Cf.* Freundlich, *Kapillarchemie*, p. 52.

supports the adsorption theory. On the other hand, Knecht showed some years ago that when the basic dye crystal violet (the hydrochloride of an organic base) is shaken up with wool or silk the dye is decomposed, the cation combining with the fibre and the anion (in this case Cl′) remaining in the solution. This result was first described as a case of double decomposition between the dye and the fibre, the dye combining with an organic acid in the fibre to form a salt, and ammonia originally associated with the fibre combining with the chlorine to form ammonium chloride. Freundlich and Neumann [1] have shown, however, that in certain cases at least the chlorine is not left in the solution as a salt, but in the form of hydrochloric acid. The exact form in which the adsorbed dye occurs on the adsorbent does not seem to have been properly established—the colour appears to indicate that it is present as a salt and not as the free base.

The process just described would at first sight appear to be an ordinary chemical change, but further investigation shows that charcoal and even glass pellets split up dyes in an exactly analogous way, the cation being adsorbed and the anion remaining in solution. It can scarcely be supposed that the charcoal or the glass enter into chemical action with the dyes. Phenomena of an exactly similar nature have already been met with in connection with the precipitation of colloids by electrolytes (p. 324), and it has been shown that they are connected with the electrical character of the colloidal particles, that ion being most largely adsorbed which carries a charge of opposite sign to that on the colloid. The splitting of basic dyes described in the present section might be accounted for on similar lines, as also the well-known fact that an " acid " fibre adsorbs more particularly basic dyes and a " basic " fibre " acid " dyes. The above is a brief outline of the adsorption theory of dyeing, but the process in any particular case is doubtless complicated by other factors, and at present is far from being understood.

It has been suggested by Bayliss and others that adsorption plays an important part in enzyme reactions; the substance acted on is first adsorbed by the colloidal enzyme particles and chemical change follows. The interesting fact that colloids

[1] *Zeitsch. physikal. Chem.*, 1909, 67, 538.

such as gelatine increased the stability of suspension colloids such as silver bromide or colloidal gold towards electrolytes may also be accounted for on the basis of adsorption. In the case under consideration it is assumed that the gelatine is adsorbed as a thin film on the surface of the particles, so that the latter do not come directly in contact with the electrolyte. It has quite recently been shown that certain dyes, more particularly erythrosine, also exert a protective action on colloidal silver bromide. Substances acting in this way are termed "protective" colloids.

CHAPTER XIII

THEORIES OF SOLUTION

General—The nature of solutions,[1] more particularly as regards the connection between their properties and those of the components, has long been one of the most important problems of chemistry. It was early recognized that the properties of a solution are very seldom indeed the mean of the properties of the components, as must necessarily be the case if solvent and solute exert no mutual influence. Thus we know that when two liquids are mixed either expansion or contraction may occur, the boiling-point of a mixture may be higher or lower than those of either of its components (p. 99), and a mixture of two liquids may have a high conductivity, although the components in the pure condition are practically non-conductors (p. 265).

The most obvious way of accounting for observations of this nature is to assume that they are connected with the formation of chemical compounds between the two components of the solution. As a matter of fact, explanations of the observed phenomena on these lines were formerly in great favour. As water was the substance most largely used as a component of solutions (as solvent), the explanation of the properties of aqueous solutions on the basis of formation of chemical compounds between water and the solute was termed the *hydrate theory of solution*. This theory appeared the more plausible as a very large number of hydrates—compounds of substances, more particularly salts, with water—are known in the solid state, thus showing that there is undoubtedly considerable chemical affinity between certain solutes and water.

[1] For simplicity, only mixtures of two components will be considered in this chapter.

In spite of the plausible nature of the hydrate theory, however, it did not prove very successful in representing the properties of aqueous solutions, and some facts were soon discovered in apparent contradiction with it. Thus, as already mentioned, Roscoe showed that the composition of the mixture of hydrochloric acid and water with minimum vapour pressure, alters with the pressure, and therefore could not be connected with the formation of a definite chemical compound of acid and water, as had previously been assumed (p. 101).

The development of the electrolytic dissociation theory, which has been discussed in the previous chapters, led to a considerable change of view with regard to the influence of the solvent on the properties of aqueous solutions. The properties of the solvent were to some extent relegated to the background,[1] and it was looked upon simply as the medium in which the molecules and the ions of the solute—the really active things—moved about freely. The fact that such great advances in knowledge have been made by working along those lines naturally goes far to justify the method of procedure.

Within the last few years, however, mainly as a result of the investigation of solutions in solvents other than water, it has come to be recognized that the solvent may play a more direct part in determining the properties of dilute solutions than some chemists were formerly inclined to suppose. Although the main properties of aqueous solutions can be accounted for without express consideration of affinity between solvent and solute, it appears probable that the latter effect must be taken into consideration in order to account for certain secondary phenomena (and possibly also in connection with ionization) (p. 345).

In the previous chapters the evidence in favour of the electrolytic dissociation theory could not be dealt with as a whole, owing to the fact that it belongs to different branches of the subject. In the present chapter a short summary of the more important lines of evidence bearing on the theory will be

[1] The properties of the solvent are, of course, all-important in determining whether a substance becomes ionized or not. But it was not found necessary to take the question of affinity into account directly, and the equations representing ionic equilibria did not contain any term referring directly to the solvent.

given, and then a brief account of the investigation of solutions in solvents other than water. Finally, after dealing with the older hydrate theory of solution, the possible mechanism of electrolytic dissociation will be considered.

Evidence in Favour of the Electrolytic Dissociation Theory—The evidence in favour of the electrolytic dissociation theory is partly electrical and partly non-electrical. The non-electrical evidence goes to show that there are more particles in dilute solutions of salts, strong acids, and bases, than can be accounted for on the basis of their ordinary chemical formulæ, and that in dilute solution the positive and negative parts of the molecule behave more or less independently. The electrical evidence goes to show that the particles which result from the splitting up of simple salt molecules are associated with electric charges, either positive or negative.

The main points are as follows :—

(*a*) If Avogadro's hypothesis applies to dilute solutions, gram-molecular (molar) quantities of different substances, dissolved in equal volumes of the same solvent, must exert the same osmotic pressure. As a matter of experiment, salts, strong acids, and bases exert an osmotic pressure greater than that due to equivalent quantities of organic substances (p. 134). The electrolytic dissociation theory accounts for this on the same lines as the accepted explanation for the abnormally high pressure exerted by ammonium chloride; it postulates that there are actually more particles present than that calculated according to the ordinary molecular formula.

(*b*) Many of the properties of dilute salt solutions are additive, that is, they can be represented as the sum of two *independent* factors, one due to the positive, the other to the negative part of the molecule. This is true of the density, the heat of formation of salts (p. 153), the velocity of the ions (p. 257), the viscosity, and more particularly of the ordinary chemical reactions for the "base" and "acid" as used in analysis (p. 311).

A very striking illustration of the independence of the properties of one of the ions in dilute solution on the nature of the other is the colour of certain salt solutions, investigated by Ostwald. He examined the solutions of a large number of

metallic permanganates, and found that all had exactly the same absorption spectra. This is exactly what is to be expected according to the electrolytic dissociation theory, the effect being exerted by the permanganate ion. Similarly, salts of rosaniline with a large number of acids in very dilute solution gave identical absorption spectra (due to the rosaniline cation), but rosaniline itself, which is very slightly ionized, gave a quite different spectrum.

Too much stress should not be laid on this criterion, however, as certain properties, *e.g.*, molecular volumes of organic compounds (p. 70) and the heat of combustion of hydrocarbons (p. 153), are more or less additive, although nothing in the nature of ionization is here assumed.

(*c*) The magnitudes of the degree of dissociation, calculated on two entirely independent assumptions—(1) that the conductivity of solutions is due to the ions alone, and not to the non-ionized molecules or to the solvent; (2) that the abnormal osmotic pressures shown by aqueous solutions of electrolytes are due to the presence of more than the calculated number of particles owing to ionization—show excellent agreement (p. 268).

(*d*) The heat of neutralization of molar solutions of all strong monoacidic bases by strong monobasic acids is 13,700 calories, in excellent agreement with the value for the reaction $H^{\cdot} + OH' = H_2O$, calculated by van't Hoff's formula from Kohlrausch's measurements of the change of conductivity of pure water with the temperature (p. 300).

(*e*) The results obtained by four entirely independent methods for the degree of ionization of water are in striking agreement, in spite of the fact that the assumed ionization is very minute (p. 299).

(*f*) The formula for the variation of electrical conductivity with dilution, obtained by application of the law of mass action to the assumed equilibrium between ions and non-ionized molecules in solution, represents the experimental results in the case of weak electrolytes with the highest accuracy (p. 273).

(*g*) As shown in the next chapter, our present views as to the origin of differences of potential at the junction of two solutions, or at the junction of a metal and a solution of one

of its salts, are based on the osmotic and electrolytic dissociation theories, and the good agreement between observed and calculated values goes far to justify the assumptions on which the formulæ are based.

Many other illustrations of the utility of the electrolytic dissociation theory are mentioned throughout the book.

Ionization in Solvents other than Water[1]—In accordance with the mode in which the subject has developed, we have up to the present been mainly concerned with aqueous solutions, and the justification for this order of treatment is that the relationships in aqueous solution are often very simple in character, as shown in detail in the last chapter. The importance of a theory would, however, be much less if it only applied to aqueous solutions, and it is therefore satisfactory that in recent years a very large number of liquids, both organic and inorganic, have been employed as solvents.

Although the progress so far made in this branch of knowledge is not great, the available data appear to show that *the rules which have been found to hold for aqueous solutions are often not applicable to non-aqueous solutions.*[2]

Some solvents, such as ethyl and methyl alcohol, acetic acid, formic acid, hydrocyanic acid and liquefied ammonia, form solutions of fairly high conductivity with salts and other substances; these are termed *dissociating* solvents (p. 132). Solutions in certain other solvents, such as benzene, chloroform, and ether, are practically non-conductors, and the solutes are often present in such solutions in the form of complex molecules. These solvents are therefore often termed *associating* solvents, but it is not certain whether they actually favour association or polymerization of the solute, or have only a slight effect in simplifying the naturally polymerized solute.

It is natural to inquire whether there is any connection between the ionizing power of a solvent and any of its other properties. It has been found that as a general rule those solvents with the greatest dissociating power have high *dielectric constants* (p. 232) (J. J. Thomson, Nernst, 1893). This observation is easily understood when it is remembered that

[1] Taylor, *Physical Chemistry* (Macmillan), pp. 583-603.
[2] *Ibid., loc. cit.*

the attraction between contrary electric charges is inversely proportional to the dielectric constant of the medium; it is evident that the existence of the ions in a free condition must be favoured by diminishing the attraction between the contrary charges. The dielectric constants of a few important solvents (liquids and liquefied gases) at room temperature are given in the table:—

Solvent.	D.C.	Solvent.	D.C.
Hydrocyanic acid . .	95	Acetone . .	21
Water	81	Pyridine . .	20
Formic acid . . .	57	Ammonia . .	16·2
Nitro benzene . .	36·5	Sulphur dioxide .	13·7
Methyl alcohol . . .	32·5	Chloroform . .	5·2
Ethyl alcohol . .	21·5	Benzene . .	2·3

The data are not usually available for an accurate comparison of the dissociating power of a solvent with its dielectric constant, as the values of μ_∞ for electrolytes in solvents other than water have been determined in only a few cases. It is important to remember that a comparison of the conductivities of solutions of the same concentration in different solvents is in no sense a measure of the respective ionizing powers of the solvents, as the conductivity also depends on the ionic velocity (p. 258). The available data are, however, sufficient to show that although there is parallelism, there is not direct proportionality between dielectric constant and ionizing power. There appears also to be some connection between the degree of association of the solvent itself and its ionizing power. The examples already given show that water, the alcohols, and fatty acids, which are themselves complex, are the best ionizing solvents. There are, however, exceptions to this as to all other rules in this section; liquefied ammonia, though apparently not polymerized, is a good ionizing solvent.

Brühl has suggested that the ionizing power of a solvent depends on what he calls subsidiary valencies (the "free affinity" of Armstrong); in other words, the best ionizing solvents are those which are unsaturated. It is by no means improbable that the dielectric constant, the degree of polymerization, and the degree of unsaturation of a solvent are in some way connected.

The ionizing power of a solvent may be partly of a physical and partly of a chemical nature. The effect of a high dielectric constant would appear to be mainly physical; on the other hand, if the effect of a solvent depends on its unsaturated character, it would most likely be chemical in character.

The Old Hydrate Theory of Solution[1]—As already mentioned, attempts have been made to account for the properties of aqueous solutions of electrolytes on the basis of chemical combination between solvent and solute. Among those who have supported this view of solution, the names of Mendeléeff, Pickering, Kahlenberg,[2] and Armstrong[3] may be mentioned.

Mendeléeff made a number of measurements of the densities of mixtures of sulphuric acid and water, and drew the conclusion that the curve representing the relation between density and composition is made up of a number of straight lines meeting each other at sharp angles, the points of discontinuity corresponding with definite hydrates, for example, H_2SO_4, H_2O; H_2SO_4, $2H_2O$; H_2SO_4, $6H_2O$ and H_2SO_4, $150H_2O$. Pickering repeated Mendeléeff's experiments, and found no sudden breaks in the density curve, but only changes in direction at certain points. He also drew the conclusion that these points correspond with the composition of definite compounds of the acid and water.

In this connection it may be recalled that the curve obtained by plotting the electrical conductivity of mixtures of sulphuric acid and water against the composition (p. 265) shows two distinct minima, at 100 per cent. and 84 per cent. of sulphuric acid respectively, corresponding with the compounds H_2SO_4 (SO_3, H_2O) and H_2SO_4, H_2O respectively. As it is a general rule that the electrical conductivity of pure substances is small, there is little reason to doubt that the 84 per cent. solution consists mainly of the monohydrate H_2SO_4, H_2O. The contention of Mendeléeff and Pickering, that aqueous solutions of sulphuric acid contain compounds of the components, is thus partially confirmed by the electrical evidence.

[1] Pickering, Watts' *Dictionary of Chemistry*, Article "Solution"; Arrhenius, *Theories of Chemistry* (Longmans, 1907), chap. iii.

[2] For a summary of Kahlenberg's views on Solution, see *Trans. Faraday Soc.*, 1905, **1**, 42.

[3] *Proc. Roy. Soc.*, 1, **81A**, 80-95 908.

There is not much reason to doubt the truth of the first postulate of the hydrate theory, that in many cases hydrates are present in aqueous solution. The hydrates are, however, in all probability more or less dissociated in solut on, and it will not usually be possible to determine the presence of definite hydrates from the measurement of physical properties. It is probable that in general the equilibria are somewhat complicated, and are displaced gradually by d lution in accordance with the law of mass action, which accounts for the experimental fact that in general the properties of aqueous solutions alter continuously with composition.

Having proved the existence of hydrates in salt solutions in certain cases, Pickering [1] attempted to account for the properties of aqueous solutions (osmotic pressure, electrical conductivity, etc.) on the basis of dissociation alone, but as his views have not met with much acceptance, a reference to them will be sufficient for our present purpose. Kahlenberg,[2] who has carried out many interesting experiments in solvents other than water, regards the electrolytic dissociation theory as unsatisfactory, and considers that the process of solution is one of chemical combination between solvent and solute. Armstrong has also attempted to account for the properties of aqueous solutions on the basis of association between solvent and solute.[3]

Although, as we have seen, cases are known in which a maximum or minimum or a change in the direction of a curve may correspond more or less completely with the formation of a compound between the two components of a homogeneous solution, this does not by any means always hold. It has already been pointed out that the curve representing the variation of the electrical conductivity of mixtures of sulphuric acid and water with the composition has a maximum at 30 per cent. of acid (p. 265). As the pure liquids are practically non-conductors, whilst the mixtures conduct, there must necessarily be a concentration, between 0 and 100 per cent. acid, at which the conductivity attains a maximum value. This maximum will clearly have no reference to the formation of a chemical com-

[1] *Loc. cit.* [2] *Loc. cit.*
[3] *Loc. cit.*, also *Encyc. Britannica*, 10th Edition, vol. xxvi., p. 741.

pound between sulphuric acid and water, since this would tend to diminish the conductivity.

Similar considerations appear to apply for other physical properties which attain a maximum value for binary mixtures. The curve representing the variation of the viscosity (internal friction) of mixtures of alcohol and water with composition shows a maximum at 0° for a mixture containing 36 per cent. of alcohol, corresponding with the composition $(C_2H_5OH)_2$, $9H_2O$, and it has therefore been suggested that the solution consists mainly of this hydrate. At 17°, however, the mixture of maximum viscosity contains 42 per cent., and at 55° rather more than 50 per cent. of alcohol. The last-mentioned mixture corresponds with the composition $(C_2H_5OH)_2$, $5H_2O$. If we accept the association view of this phenomenon, it must be assumed at 0° the solution contains a hydrate $(C_2H_5OH)_2$, $9H_2O$, and at 55° a hydrate $(C_2H_5OH)_2$, $5H_2O$, and that at intermediate temperatures the hydrates with 6, 7, and 8 H_2O exist—which does not appear very probable.

Now, Arrhenius has shown that as a general rule the addition of a non-electrolyte raises the viscosity of water. Therefore, if the viscosity of the non-electrolyte is less than, or only slightly exceeds that of water, the curve obtained by plotting viscosity against the composition of the mixture must necessarily attain a maximum at some intermediate point. Why mixtures of two liquids have often a higher viscosity than either of the pure liquids is not known, no general agreement having yet been reached on this and allied questions.[1]

Mechanism of Electrolytic Dissociation. Function of the Solvent—The fundamental difference between association theories of solution, as discussed in the last section, and the electrolytic dissociation theory is that the advocates of association entirely reject the postulate of the independent existence of the ions. As, however, the different theories of association unaccompanied by ionization have so far proved quite inadequate to account quantitatively for the behaviour of aqueous solutions, whilst

[1] Compare Senter, *Proc. Chem. Soc.*, 1909, 292. For evidence in favour of the association view of this phenomenon, compare Dunstan, *Trans. Chem. Society*, 1907, **91**, 83; Dunstan and Thole, *ibid.*, 1909, **95**, 1556.

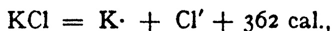
the electrolytic dissociation theory not only affords a satisfactory quantitative interpretation of the more important phenomena observed in solutions of electrolytes (Chap. x.), but has led to discoveries of the most fundamental importance for chemistry, it is not surprising that the electrolytic dissociation theory has now met with practically universal acceptance. It is very likely that as a result of further investigation the theory may require modification in some subsidiary respects, but its general validity appears no longer doubtful.

We are now in a position to discuss the possible mechanism of electrolytic dissociation, *i.e.*, the factors concerned in the conversion of a non-ionized salt into ions when dissolved in water or other ionizing solvent. In this connection two points of importance must be kept in mind: (1) There is a more or less complete parallelism between the ionizing power of a solvent and certain of its properties, such as the magnitude of the dielectric constant and its degree of polymerization; (2) the sum of the energy associated with the ions is usually not very different from that associated with the non-ionized molecules in solution. The first point has already been fully dealt with. The energy relations in the process of ionization will now be briefly considered.

As such elements as potassium and chlorine give out a large amount of heat when they combine to form potassium chloride, it seems at first sight as if the splitting up of potassium chloride into $K^{\cdot}$ and Cl' ions must absorb a large amount of heat. Although it has to be borne in mind that the salt is not split up into its component elements (a process which certainly absorbs a large amount of heat) but into $K^{\cdot}$ and Cl' ions, of the energy content of which little is known, it is nevertheless probable that the process of ionization does involve a taking up of energy, as the following considerations show.

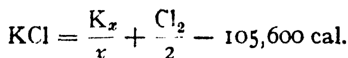
It has already been pointed out that the heat of ionization (the heat given out when a mol of a non-ionized salt in solution is completely ionized) may be calculated by the van't Hoff formula connecting heat given out with displacement of equilibrium, when the equilibrium at two near temperatures is known (p. 290). The available data indicate that the heat of ionization is small, and may be positive or negative. According

to Arrhenius, the energy equation for the ionization of *dissolved* potassium chloride is as follows :—



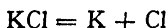
$$KCl = K^{\cdot} + Cl' + 362 \text{ cal.},$$

the heat of ionization being thus exceedingly small. On the other hand, when potassium chloride is formed from its elements, 105,600 cal. are given out for gram-equivalent quantities, hence the energy equation for the decomposition of potassium chloride into metallic potassium and free chlorine is



$$KCl = \frac{K_x}{x} + \frac{Cl_2}{2} - 105,600 \text{ cal.}$$

The further separation of metallic potassium and free chlorine into *uncharged* atoms would probably absorb still more heat, so that the reaction



$$KCl = K + Cl$$

must absorb a very large amount of heat. On the other hand, we have just seen that in the splitting up of the salt into *charged* atoms—the ions—a little heat is actually given out. It seems, therefore, that the process of ionization must be attended by some exothermic reaction, which more than compensates for the heat presumably absorbed in splitting up the molecules.

Up to the present no definite conclusion has been arrived at as to the source of the energy in question. Some of the possibilities are as follows :—

(*a*) As the molecule splits up into particles charged with electricity, the energy in question may come from some interaction between electricity and matter. On this point nothing can be said with certainty in the present state of our knowledge.[1]

(*b*) The energy may result mainly from combination between the ions and water. Van der Waals[2] (1891) has suggested that ionization in aqueous solution is essentially a hydration process; he considers that it is the affinity of the ions for the solvent which effects the break-up of the molecule, and that the energy required for ionization comes from the heat of hydration of the ions.

[1] *Cf.* Ostwald, Fitzgerald, *British Association Reports*, 1890.

[2] *Zeitsch. physikal. Chem.*, 1891, **8**, 215. *Cf.* Bousfield and Lowry, *Trans. Faraday Soc.*, 1907, **3**, 1.

(*c*) Dutoit, arguing from the parallelism between the polymerization of the solute and its ionizing power, and assuming that the process of solution is attended with partial simplification of the solute molecules, has suggested that the energy is obtained from the depolymerization in question.

The suggestion of van der Waals finds a certain amount of support from recent investigations on solvents other than water. Carrara[1] considers that the ions are produced as a consequence of the chemical affinity between the two parts of the molecule and the solute, and that in consequence of the high dielectric constant in ionizing media, they, along with their associated solvent molecules, are kept in the ionic condition once they are formed.

It should, however, be remembered that this suggestion as to the mechanism of ionization, although interesting and suggestive, is little more than a plausible speculation, and that there are many points about this process which are very imperfectly understood.

Newer Theories regarding Strong Electrolytes—Within the last few years the problem of the anomalous behaviour of strong electrolytes has been brought much nearer to solution. It has become clear that the properties of strong electrolytes cannot be represented in terms of a degree of dissociation measured by the ratio of conductivities μ_v/μ_∞ (p. 267). A great deal of attention has been devoted to the exact determination of the thermodynamical properties of solutions, and the results have been expressed in terms of the concept of activity introduced by G. N. Lewis.[2] The "activities" are expressions of the partial free energies of substances in solution and the activities of the components of a solution are not strictly proportional to their respective molecular concentrations. The deviation from the laws of a perfect gas or a perfect solution may be conveniently expressed by the activity coefficient, γ, the ratio of activity, a, to concentration, c, which is the factor by which the concentrations have to be multiplied in order to make the law of mass action applicable to actual as distinguished from ideal solutions. The activities of all molecules and ions approach

[1] *Loc, cit.*, p. 417.

[2] Cf. Lewis and Randall, *Thermodynamics*. The McGraw Hill Book Co. (1923).

proportionality to their concentrations as their concentrations approach zero.

The activity coefficients of a large number of substances have been determined from vapour pressure, freezing-point and E.M.F measurements, and the results obtained by the different methods are in good agreement. In the case of strong electrolytes the activity coefficient (which is unity at zero concentration) diminishes at first with increasing concentration, reaches a minimum and rises again, becoming greater than unity at high concentrations. These results are of course independent of any theory which may be put forward to account for the deviations from the behaviour of ideal solutions.

As has already been mentioned, it is now generally accepted that in the case of strong electrolytes the degree of dissociation cannot be obtained by applying the formula $\alpha = \mu_v/\mu_\infty$ which holds so accurately for weak electolytes. The view has gained ground that strong electrolytes are completely or almost completely ionized in solution and that the alteration of equivalent conductivity with concentration is due mainly to changes in the electrical forces between the ions. The Debye-Hückel theory of interionic forces postulates that owing to electrical attraction every ion is surrounded by an excess of ions of opposite charge. The theory has been applied to osmotic properties and also to electrical conductivities with fairly satisfactory results. We will here consider only the application to electrical conductivities. Assuming Stokes' law, Debye and Hückel deduce the formula for dilute solutions

$$\lambda_\infty - \lambda_c = \lambda_\infty(K_1 w_1 + K_2 b)\sqrt{2c} \quad . \quad . \quad (1)$$

where λ_∞ and λ_c are the equivalent conductivities at infinite dilution and at concentration c, and $w_1 = \frac{1}{2}(l_a/l_c + l_c/l_a)$, l_c and l_a being the mobilities of cation and anion, b the mean ionic radius, K_1 and K_2 constants depending on the temperature and dielectric constant of the medium. When an ion is moving through a solution a finite time is required for the redistribution of the ions in accordance with the Debye-Hückel theory (period of relaxation) and there will always be excess of ions of the opposite sign in the rear, hence the ion will be subject to a retarding force. Further, since ions of different sign are moving in opposite directions and dragging with them a certain amount of solvent the viscous resistance to the motion of an ion will

be greater than if the other ion were at rest. The term $K_1 w_1$ in equation (1) represents the diminution of conductivity due to the unsymmetrical distribution of the ions, $K_2 b$ that due to the viscosity effect.

The Debye-Hückel theory has been tested by numerous investigators and its general validity may be regarded as established, although it may require modification in minor respects. Onsager [1] has recently introduced a correction by taking account of the Brownian movement of the ions. As it happens, this leads to a much simpler equation than the original one of Debye and Hückel. The mean radius of anion and cation in the Debye-Hückel equation is eliminated and a knowledge of the individual ionic mobilities is not required. The equation therefore contains no adjustable constant and is well adapted for testing the theory. When numerical values for universal constants are inserted the equation takes the form for uni-univalent electrolytes :

$$\lambda_c = \lambda_\infty - \left[\frac{5{\cdot}78 \times 10^5}{(DT)^{\frac{3}{2}}} \cdot \lambda_\infty + \frac{58{\cdot}0}{(DT)^{\frac{1}{2}}\eta}\right]\sqrt{2c},$$

where D represents the dielectric constant at T° abs., and η represents the viscosity. For many aqueous and alcoholic solutions the equation predicts with considerable accuracy the relationship between conductivity and concentration.

It is probable that electrolytic dissociation is not complete for solutions of strong electrolytes in water even in moderately dilute solutions (0·3 normal). Nernst [2] accounts satisfactorily for the heats of dilution of strong electrolytes in water by assuming incomplete dissociation in accordance with the law of mass action in addition to the effects due to interionic attraction (Debye-Hückel theory).

Martin [3] has reached a similar conclusion from the results of electrical conductivity measurements of solutions of the iodides of lithium sodium and potassium, of lithium bromide and of silver nitrate in benzonitrile. When a correction is applied for interionic attraction effects he finds that the simple Ostwald dilution law applies. It would appear, therefore, that when allowance is made for interionic attraction effects even strong electrolytes obey the law of mass action.

[1] Onsager, *Physikal. Zeitsch.*, 1926, **27**, 338; 1927, **28**, 277.
[2] Nernst, *Z. Electrochem.*, 1927, **33**, 428.
[3] Martin, *J. Chem. Soc.*, 1928, 3270.

CHAPTER XIV

ELECTROMOTIVE FORCE

The Daniell Cell. Electrical Energy—The Daniell cell consists essentially of a large beaker or other vessel, containing a small porous cell. In the outer vessel, surrounding the porous cell, is a solution of zinc sulphate in which dips a rod of zinc, and the porous pot contains a solution of copper sulphate, in which dips a plate of copper. When the copper plate is connected to the zinc by a wire, an electric current flows through the wire. As positive electricity passes in the wire from copper to zinc, the copper is termed the positive, the zinc the negative pole. An examination of the cell will show that when the current is flowing, zinc is being dissolved at the negative pole, and copper is being deposited on the positive pole. If, instead of copper sulphate, the porous pot contains dilute sulphuric acid, hydrogen is given off *at the surface of the copper* when the zinc and copper are connected. It is, therefore, clear that the chemical change which gives rise to the current is the dissolving of zinc in sulphuric acid, represented by the equation $Zn + H_2SO_4 = ZnSO_4 + H_2$, and that in the Daniell cell the hydrogen is got rid of by reducing copper sulphate in the porous pot, the change being represented by the equation $CuSO_4 + H_2 = H_2SO_4 + Cu$. Combining the two equations, the chemical changes taking place while a Daniell cell is working are represented by the equation



$$Zn + CuSO_4 = ZnSO_4 + Cu,$$

which may be written



$$Zn + Cu^{\cdot\cdot} + SO_4'' = Zn^{\cdot\cdot} + SO_4'' + Cu,$$

or more concisely,



$$Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu,$$

that is, zinc changes from the metallic to the ionic form, and at the same time copper changes from the ionic to the metallic form.

The Daniell cell may be looked upon as a machine for the conversion of chemical to electrical energy, and it is of great interest to inquire whether chemical energy is transformed into the *equivalent amount* of electrical energy, or whether other kinds of energy, such as heat, are also produced in the cell. This question can at once be settled by determining the heat equivalent, in calories, of the chemical energy transformed when 1 mol of copper in solution is displaced by zinc, and comparing it with the electrical energy (measured in calories) obtained during the process.

From Thomsen's measurements (p. 148) the displacement of 1 mol of copper in dilute solution by zinc is associated with a heat development of 50,130 calories. The electrical energy in volt-coulombs is, as has already been pointed out, the product of the electromotive force E in volts and the quantity of electricity in coulombs. E for the Daniell cell is about 1·09 volts at room temperature. From Faraday's law we know further that the liberation of a gram-equivalent of positive or negative ions is associated with the passage of 96,500 coulombs, hence, as zinc and copper are bivalent, the reaction



$$Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu$$

is associated with the passage of 2 × 96,500 coulombs. The electrical energy, *in calories* (1 volt-coulomb = 0·2391 calories), is therefore given by[1]

$$ECt = 1{\cdot}09 \times 2 \times 96{,}500 \times 0{\cdot}2391 = 50{,}300 \text{ cal.}$$

as compared with 50,130 calories, the heat equivalent of the chemical change which has taken place in the cell. The excellent agreement between observed and calculated values shows that in this case the assumption that the chemical energy is transformed completely to electrical energy is approximately fulfilled.

It should be remembered that in an actual cell other chemical

[1] C is the current, t the time, and Ct therefore the quantity of electricity.

changes may accompany the primary ones; for example, those giving rise to the so-called E.M.F. of polarization (p. 396). In comparing the heat equivalent of the main chemical action taking place in the cell with the electrical energy obtained, such changes must, of course, be allowed for. In the Daniell cell, however, there is no polarization, and the only reaction which takes place to any appreciable extent is the displacement of copper by zinc, as has already been assumed. In this chapter we are mainly concerned with such non-polarizable cells.

On account of the excellent agreement between the amount of chemical energy expended and the electrical energy generated in the Daniell cell, it was at first thought that the transformation of chemical to electrical energy in all cells is practically complete, but further investigation showed that this is by no means always the case. As indicated above, the question can readily be investigated for a non-polarizable element by comparing the heat equivalent, Q, of the chemical change taking place in the element with the electrical energy generated while known quantities of the reacting substances are being transformed. The electrical energy may conveniently be measured as follows: The poles of the cell are connected by a thin wire of high resistance, R. If r is the internal resistance of the cell, the electrical energy generated in unit time is given by

$$EC = C^2 (R + r).$$

Now R may easily be made so large compared with r that the amount of electrical energy converted to heat in the cell is negligible in comparison with that transformed in the outer wire. If then the current is measured and R is known, the quantity of electrical energy produced by the cell in unit time is known, and hence that produced when $n \times 96{,}500$ coulombs have passed round the circuit. This quantity of electrical energy is obtained during the chemical transformation of n equivalents of the cell material, and may be compared with Q, the heat given out when the chemical change takes place in a calorimeter.

When a Daniell cell is examined in this way, it is found, as has already been pointed out, that the electrical energy is practically equal to Q, the heat equivalent of the chemical energy. There are, however, elements in which the electrical energy thus

expended in the outer wire is *less* than the heat of the reaction; in this case part of the chemical energy is expended as heat in the cell. In other elements, however, the electrical energy, ECt, is *actually greater than the heat of reaction*, Q, so that the element, while working, *takes heat from its surroundings and transforms it into electrical energy.*

Relation between Chemical and Electrical Energy—The exact relationship between the chemical energy transformed and the maximum energy obtainable electrically in a reversible galvanic element can be obtained on thermodynamical principles by means of a cyclic process. The formula expressing the relationship (Willard Gibbs, 1878; Helmholtz, 1882), usually known as the Helmholtz equation, is as follows:—

$$nFE - Q = nFT\frac{dE}{dT} \quad . \quad . \quad . \quad (1)$$

or

$$E = \frac{Q}{nF} + T\frac{dE}{dT} \quad . \quad . \quad . \quad . \quad (2)$$

where E is the E.M.F. of the cell, Q is the heat equivalent of the chemical change for molar quantities, expressed in electrical units, F is 96,500 coulombs, T is the absolute temperature at which the cell is working, and n is the valency, or the number of charges carried by a mol of the substances undergoing change. By dE/dT is meant the rate of change of the E.M.F. of the cell with temperature—in other words, the temperature coefficient of the E.M.F.

The Helmholtz formula is simply a direct application of the free energy equation

$$A - U = T\frac{dA}{dT} \quad . \quad . \quad . \quad . \quad (3)$$

to a chemical change taking place in a galvanic cell. In the latter formula, U represents the total diminution of energy in a reacting system, and A is the available or free energy, that is, the maximum proportion of the total change of energy, U, which can be transformed into work (p. 157). In order to obtain formula (1) Q, the heat of reaction measured calorimetrically, is substituted for U in the free energy equation, and for A, the free energy, is substituted nFE, the maximum energy obtain-

able electrically for molar quantities.[1] dA/dT in the free energy equation then becomes $nFTdE/dT$ (n and F being constants), equation (1) being thus obtained. The equation should be remembered in the second form.

From the first form of the Helmholtz equation, some very important conclusions can be drawn as to the behaviour of reversible elements :—

(*a*) If dE/dT is positive, that is, if the E.M.F. of the element increases with temperature, the electrical energy, nFE, is greater than the heat of reaction, Q, and the cell takes heat from its surroundings while working.

(*b*) If dE/dT is negative, that is, if the E.M.F. of the element diminishes as the temperature rises, the heat of reaction, Q, is greater than the electrical energy, nFE, and the cell warms while working.

(*c*) If the E.M.F. does not alter with change of temperature (as is approximately the case in a Daniell cell), the heat of reaction, Q, is equal to the electrical energy, and the cell does not alter in temperature while working.

(*d*) At absolute zero, that is, $T = 0$, the right-hand side, and therefore also the left-hand side, of equation (1) becomes zero, hence at the absolute zero the heat of reaction (diminution of chemical energy) is always equal to the maximum electrical energy obtainable (or in general to the free energy, *cf.* p. 159).

The applicability of the Helmholtz formula to chemical changes which can be brought about reversibly in a galvanic element has been proved experimentally by Jahn and others. As an example, we will consider a cell made up of zinc and silver in contact with solutions of the respective chlorides. The observed E.M.F. of such a cell at 0° is 1·015 volts, and the electrical energy in *calories* for the transformation of 1 mol of the reacting substances is given by $nFE = 1{\cdot}015 \times 96{,}500 \times 2 \times 0{\cdot}239 = 46{,}840$ calories. The heat of reaction (due to the displacement of the equivalent amount of silver from solution by 1 mol of zinc) is 52,046 cal. Hence, as the heat of

[1] When the change taking place in a galvanic cell is reversible, then, according to the second law of thermodynamics, the electrical energy obtained, nFE, is the maximum work obtainable from the change and is therefore a measure of the free energy or chemical affinity of the reaction (p. 159).

reaction is greater than the electrical energy, the temperature coefficient of the E.M.F. is negative, and is given by the formula

$$\frac{dE}{dT} = \frac{nFE - Q}{nFT} = \frac{(46,840 - 52,046)\ 4 \cdot 184}{2 \times 96,540 \times 273} = -\ 0 \cdot 00041 \text{ (volts}$$

per degree) in excellent agreement with the experimental value, $-\ 0 \cdot 00040$. As the value of dE/dT is required in volts, the energy in the above equation is necessarily represented in volt-coulombs (calories $\times$ 4·183).

In order further to illustrate the above statements, which are of fundamental importance for our work, they will now be repeated in a somewhat different form. The quantities of energy given in the following paragraphs refer to molar quantities throughout.

When a chemical change takes place without the performance of external work, the total change of energy, U, is equal to the heat of reaction, Q, measured in a calorimeter.

When the same reaction takes place in a battery the poles of which are connected by a thin wire, the whole apparatus, including the connecting wire, being enclosed in a calorimeter, the heat developed in the latter is again Q for molar quantities transformed, the electrical energy in the connecting wire being degraded to heat.

When the cell is in the calorimeter, and the thin connecting wire outside, there are three possible cases :—

(*a*) If the heat of reaction, Q, is equal to the maximum electrical energy obtainable, nFE, and if further the resistance of the cell is zero (in practice, very low) no heat will be developed in the calorimeter, and the equivalent of Q calories of electrical energy will pass round the external wire.

(*b*) If the heat of reaction is greater than the maximum electrical energy obtainable, heat will be developed in the calorimeter as well as in the external circuit.

(*c*) If the heat of reaction is less than the maximum electrical energy heat will be *absorbed* in the calorimeter, and the heat equivalent of the electrical energy in the outer circuit will be greater than Q (provided that the resistance of the cell is negligible).

It has already been pointed out that the maximum work can only be obtained by carrying out a process reversibly, and therefore the Helmholtz formula only applies to elements in which the process can be effected reversibly. This means that if an element such as the Daniell is giving out electrical energy at an E.M.F. represented by E, it can be restored to its initial condition by passing through it, at an E.M.F. only just exceeding E, a quantity of electrical energy equal to that given out. In order that an electrochemical process should be completely reversible, the energy should be given out and taken in at the same potential, which in practice is impossible. A completely reversible process is therefore only an ideal case, which can be more or less completely attained to in actual practice.

Many electrochemical processes are irreversible, more particularly those in which gases are evolved. For example, a Daniell cell in which the copper sulphate solution is replaced by sulphuric acid is irreversible, as, owing to the escape of hydrogen, it cannot be restored to its former condition by passing a current in the contrary direction.

Measurement of Electromotive Force—The difference of potential between the two poles of a cell may have very different values according to the conditions of measurement. If the poles are connected by a wire of very high resistance, R, and the resistance of the cell is r, the fall of potential in the wire is CR and in the cell Cr. Since $E = C(R + r)$, it is clear that the fall of potential CR in the outer circuit is only equal to E when the resistance R is infinitely large compared with r. It is therefore easy to understand why the resistance of volt-meters (instruments on which the difference of potential between two points can be read off directly in volts) is always very high. A further complication in measuring the E.M.F. of a cell while working is that in many cases the products of electrolysis accumulate on the electrodes, and set up an electromotive force in the opposite direction to the E.M.F. of the cell itself—a phenomenon which is termed polarization.

These difficulties are avoided by measuring the difference of potential between the poles of a cell *when the circuit is open*, that is, when the cell is not sending a current. In the present chapter, the symbol E stands for the E.M.F. of the cell on open

circuit. The effect of completing the circuit will be dealt with more fully at a later stage.

The E.M.F. of a cell on open circuit is most conveniently measured by the Poggendorff compensation method. The principle of the method is that the E.M.F. of the cell is just compensated by an equal and opposite E.M.F. so that no current passes, and the measurement consists in altering an adjustable E.M.F. till the above condition is fulfilled. The arrangement of the apparatus for this purpose is shown in Fig. 40. A is a lead accumulator, or other source of *constant* E.M.F., which is connected to the two ends of a uniform wire BC, which may conveniently be a metre in length. The cell E, the E.M.F. of

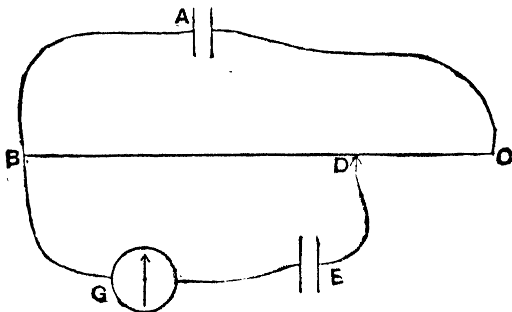


FIG. 40.

which is to be measured, is connected through a sensitive galvanometer G and a tapping key to one end of the bridge wire at B, and on the other to a sliding contact. The slider is moved along the wire until a position D is found at which, when contact is made, no current passes through the galvanometer. A standard Weston cell is then substituted for the cell E and the new balance point, D′, determined as before. The E.M.F. of the cell is then given by $E = 1{\cdot}0183 \times BD/BD'$, as the E.M.F. of the Weston cell at room temperature is 1·0183 volts. It is best to arrange a switch so that alternate readings for the cell E and the standard cell can be made rapidly, thus avoiding errors due to changes in the E.M.F. of the accumulator during the measurements. As null instrument, for showing that the point of balance has been

reached, by the fact that a current no longer passes when contact is made, a high resistance galvanometer or a capillary electrometer (p. 378) may be used; the former may be made the more sensitive, but the latter is in many respects very convenient.

The measurement of the E.M.F. of a cell on open circuit may also be made by means of the quadrant electrometer, the deflection of the needle being proportional to E, but this method is in some respects less advantageous than the compensation method.

In general, the observed E.M.F. of a cell on closed circuit is less than that on open circuit; this is due, as already indicated, to polarization effects and to the effect of the internal resistance of the cell.

Standard of Electromotive Force. The Cadmium Element—The importance of obtaining a cell, the E.M.F. of which is accurately known, has already been pointed out. The cadmium element, sometimes called the Weston element,[1] which is most largely in use for this purpose, will now be described.

The cell itself consists of an H-shaped glass vessel, the side tubes are closed at their lower ends, and platinum wires, sealed in the glass, pass through near the lowest points of the side tubes. In the bottom of one of the tubes is a layer of mercury about 1 cm. deep, above which is a paste (5 mm.) of mercurous sulphate, which has been carefully freed from traces of mercuric salt. In the bottom of the other side tube is a layer of cadmium amalgam (about 13 per cent. of cadmium quite free from zinc) above which is a paste (5 mm.) of cadmium sulphate, prepared by rubbing together in a mortar water and crystallized cadmium sulphate, and pouring off the clear saturated solution. The remainder of the cell on both sides, as well as the connecting tube, contains a saturated solution of cadmium sulphate, in which are moderately large crystals of the solid salt, and both side tubes are hermetically closed at the top, a small air space being left to allow of expansion. When required as a standard of E.M.F., connection is made by means of the platinum wires, which are in contact with the mercury and amalgam respectively.

[1] The true Weston element differs slightly from that here described.

The great advantage of the cadmium element is that its E.M.F. is practically independent of temperature. The E.M.F. at temperatures from 0° to 30° is as follows :—

0°	5°	10°	15°	20°	25°	30°
1·0189	1·0189	1·0189	1·0188	1·0186	1·0184	1·0181 volts,

the mercury being positive.

When in use the element should only be allowed to send a very small current for a very short time; if this condition is not observed the E.M.F. soon alters owing to polarization.

The mode of action of the element will be understood when the section on the calomel electrode has been read.

The corresponding cell with zinc amalgam and zinc sulphate instead of cadmium amalgam and cadmium sulphate, was formerly in general use as a standard element under the name of the Clark cell. Its chief drawback is that the E.M.F. alters considerably with temperature. The E.M.F. of the Clark cell is given by the equation

$$E = 1{\cdot}4328 - 0{\cdot}00119\,(t - 15°) - 0{\cdot}000007\,(t - 15)^2.$$

Solution Pressure—In a former section it has been shown that the relation between chemical and electrical energy in a voltaic cell is given by the Helmholtz formula

$$E = \frac{Q}{nF} + T\frac{dE}{dT}.$$

This formula has been deduced from considerations which are quite independent of any assumption as to the *mechanism* of the establishment of differences of potential in a cell, and therefore holds quite independently of any theory as to the origin of differences of potential. A much deeper insight into this problem is gained on the basis of a theory due to Nernst, based on the theory of electrolytic dissociation, and this theory will now be considered.

Every substance has a tendency to change from the form in which it actually exists to another form. Water, for example, has a tendency to pass into vapour, and if the vapour be continually removed from its surface, a definite quantity of water

will change completely to vapour. The tendency in question is measured by the vapour pressure of the water, and is constant at constant temperature. Further, a solid, such as sugar, when brought in contact with water, tends to pass into solution, and from the analogy with water and water vapour we may say that sugar has a definite *solution pressure*, which is constant at constant temperature, since the active mass of a solid, such as sugar, is constant (p. 184). On the other hand, the dissolved sugar has a tendency to separate in the solid form, which is the greater the higher the concentration, and when the solution is supersaturated the tendency to the separation of solid sugar is greater than the tendency of the latter to pass into solution. From the considerations advanced on p. 109, it is clear that *the pressure of the sugar in solution is its osmotic pressure*, and under definite conditions sugar will enter into or separate from solution according as its solution pressure is greater or less than its osmotic pressure.

These considerations, in conjunction with the ionic theory, enable us to express the E.M.F. at a junction metal/solution in terms of solution pressure and osmotic pressure. If a metal is dipped into water it tends to dissolve, in consequence of its solution pressure, P, and as it can only do so in the ionic form, it sends a certain number of positive ions into solution. The solution thus becomes positively charged, and the metal, which was previously neutral, becomes negatively charged in consequence of the loss of positive ions. This process will proceed until, by the accumulation of positive electricity in the solution, the latter becomes so strongly positive that it prevents the passage of more positive ions into solution. As the charge on the ions is so great, this process comes to a standstill when the amount of ions gone into solution is still excessively small, too small to be detected by analytical means.

The state of affairs is rather different when a metal is dipped into a solution of one of its salts, *e.g.*, zinc in a solution of zinc sulphate. In this case there are already positive metallic ions in the solution, which tend to resist the entrance of further positive ions, and what actually occurs will clearly depend upon the *relative values of the solution pressure*, P, *of the metal and the osmotic pressure*, p, *of the ions in solution.* There are, in fact,

three possible cases, which are represented diagrammatically in the accompanying figure :—

(*a*) If $P > p$, the metal sends ions into the solution until the accumulated electrostatic charges prevent further action; the metal is then negatively and the solution positively charged.

(*b*) If $P < p$, the positive ions from the solution deposit on the metal until the electrostatic charges prevent further action; the metal is then positively and the solution negatively charged.

(*c*) If $P = p$, no change occurs, and there is no difference of potential between metal and solution.

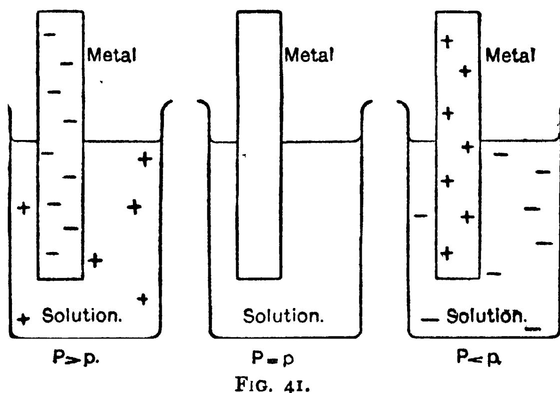


FIG. 41.

As will be shown later, the solution pressures of the different metals are very different. Those of the alkali metals, zinc, iron, etc., are so great that they always exceed the osmotic pressures of their respective solutions (which cannot be increased beyond a certain point owing to the limited solubility of the salts), and these metals are, therefore, always negatively charged with reference to their solutions. On the other hand, the solution pressure of mercury, silver, copper, etc., is so small that they become positively charged, even in very dilute solutions of their respective salts.

Calculation of Electromotive Forces at a Junction Metal/Salt Solution—Provided that the changes at the junction of an electrode with a solution are reversible, the E.M.F. at the junction can readily be calculated in terms of the solution

pressure, P, of the metal and the osmotic pressure, p, of the solution. This can perhaps be done most simply by calculating the maximum work obtainable when a mol of the electrode metal is brought from the pressure P to the lower pressure p, (1) osmotically, (2) electrically. If a mol of a dissolved substance is brought reversibly from the pressure P to p the work gained (in this case the osmotic work) is (*cf.* p. 139).

$$A = RT \log_e \frac{P}{p}.$$

Further, the dissolving of 1 equivalent of a metal is associated with 96,500 coulombs, and that of a mol of a metal of valency n with 96,500 n coulombs. The work done is the product of the E.M.F. E in volts and the quantity of electricity, 96,500 n coulombs. Equating the osmotic and electrical work, we have

$$n\, 96{,}500\, E = RT \log_e P/p$$

$$\text{or} \qquad E = \frac{RT}{96{,}500n} \log_e \frac{P}{p} \quad . \quad . \quad . \quad (1)$$

In order to obtain E in volts, R must be expressed in electrical units (volt-coulombs). If, at the same time, the change is made to ordinary logarithms (by multiplying by 2·3026) the above equation becomes

$$E = \frac{2{\cdot}3026 \times 1{\cdot}99 \times 4{\cdot}183\, T}{96{,}500n} \log_{10} \frac{P}{p} = \frac{0{\cdot}0001983\, T}{n} \log_{10} \frac{P}{p}.$$

The numerical values of 2·3026 RT/F at 0°, 18°, 25° and 30° are as follows :—

Absolute temperature	273°	273+18°	273+25°	273+30
Value of 2·3026 RT/F	0·0541	0·0577	0·0591	0·0601

At room temperature (15-20°) the value of the expression in question is about 0·058, and the general formula becomes

$$E = \frac{0{\cdot}058}{n} \log_{10} \frac{P}{p} \quad . \quad . \quad . \quad (2)$$

which should be remembered. It is clear from the form of the above equation that a tenfold increase or decrease in the

osmotic pressure of the ions of the metal will produce a change of E.M.F. of 0·058 volts for a univalent metal, and $0 \cdot 058/n$ volts for a n-valent metal, at room temperature.

Differences of Potential in a Voltaic Cell—Two such electrodes as have just been described may be combined together to form a voltaic cell. This may be done in many ways, but a convenient arrangement is that for the Daniell cell represented in Fig. 42, in which the solutions are separated by a porous partition, A, which prevents convection, but allows the current to pass. When the poles are placed in the respective solutions, the zinc becomes negatively charged, since $P_1 > p_1$; on the other hand, the copper becomes positively charged as $p_2 > P_2$. As already explained, the solution and precipitation soon come to a standstill because of the accumulation of electrostatic charges. If, however, the electrodes are connected by a wire, the contrary charges neutralize each other through the wire, and in the solution more metal can then be dissolved and deposited respectively (as there are no longer any opposing forces), the corresponding charges are again neutralized, and so on. The neutralization of charges through a conductor corresponds with the passage of a current.

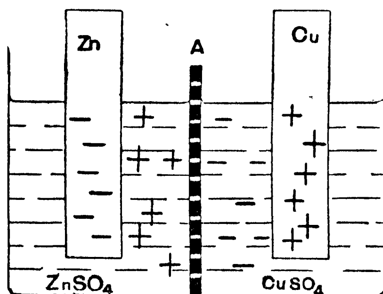


FIG. 42.

The general question as to the seat of the E.M.F. in such a cell as the Daniell has now to be considered. If the poles of the cell are connected by a wire of metal, M, there are no less than five junctions at which there may be contact differences of potential; two metallic junctions, Zn/M and M/Cu, two metal/solution junctions, $Cu/CuSO_4$ and $Zn/ZnSO_4$, and one liquid junction, $ZnSO_4/CuSO_4$. The question as to whether there are contact differences of potential at the junction of two metals gave rise to great difference of opinion, and the controversy lasted the greater part of last century. It is now generally

agreed, however, that if there are such differences they are exceedingly small in comparison with those of the junctions metal/salt solution. The difference of potential at the liquid junction is of much more importance and can be calculated by Nernst's theory (p. 381). It also is small in comparison with those at the liquid/metal junctions, and may therefore be left out of account for the present.

The distribution of differences of potential in the Daniell cell *with open circuit* is represented in Fig. 43 (*a*), the ordinates representing the potentials of the different parts of the circuit. The horizontal lines, AB, CD, DE, and FG, illustrate the very important fact that the copper, the zinc, and the solutions are

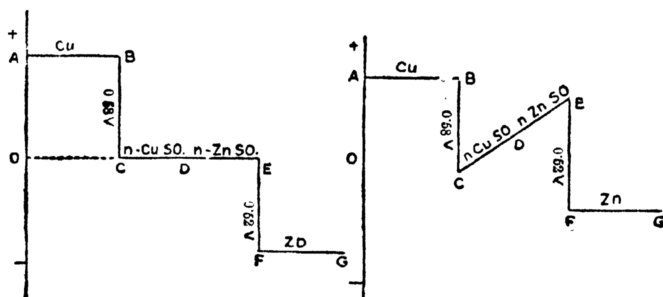


FIG. 43.

each of a definite constant potential, and the ordinates, BC and EF, that there are *sudden* alterations of potential at the junctions metal/solution. For simplicity the solutions of zinc sulphate and copper sulphate are represented as being at the same potential, which is only approximately true. It is assumed for the present that the difference of potential between copper and N copper sulphate solution is 0·585 volts, the copper being positive, and that the potential difference, $Zn/nZnSO_4$, is 0·52 volts, the metal being negative. The total difference of potential between zinc and copper on open circuit is thus $0{\cdot}585 + 0{\cdot}52 = 1{\cdot}105$ volts.

When the circuit is closed by connecting the copper and zinc by a wire of fairly high resistance, R, the distribution of potential in the cell is as shown in Fig. 40 (*b*). The sudden changes of

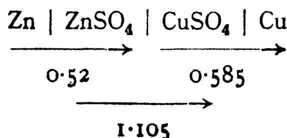
potential at the junctions $ZnSO_4/Zn$ and $CuSO_4/Cu$ are of the same magnitude as before, but the difference of potential between the zinc and copper, measured by the vertical height, AG, is much less than on open circuit. This is owing to the fall of potential in the cell owing to the resistance of the electrolyte, so that the solution in contact with the zinc is at a higher potential than that in contact with the copper, as represented by EDC. If C is the current passing through the cell, and r is the resistance of the electrolyte, the E.M.F. of the cell on closed circuit is given by $E = CR + Cr$, and CR, the fall of potential in the external wire (represented in the figure by the vertical distance AG), approaches the more nearly to the E.M.F. of the same cell on open circuit the greater R is compared with r (compare p. 355).

The E.M.F. of such a combination as the Daniell cell is the *algebraic* sum of the E.M.F.'s at the two junctions, and is represented by the formula

$$E = E_1 - E_2 = \frac{0{\cdot}058}{n}\left(\log_{10}\frac{P_1}{p_1} - \log_{10}\frac{P_2}{p_2}\right).$$

Where P_1 and P_2 are the solution pressures of zinc and copper respectively, p_1 represents the osmotic pressure of the zinc ions in the solution, and p_2 that of the copper ions. The values of p_1 and p_2 are therefore known, but the absolute values of the solution pressures P_1 and P_2 are unknown. The $-$ sign of E_2 is due to the fact that at that junction ions are leaving the solution.

In obtaining E as the algebraic sum of the differences of potential E_1 and E_2 at the two junctions, it is naturally of the utmost importance to take the values of E_1 and E_2 with their proper sign. Perhaps the best method of avoiding errors in this connection is to consider the tendency of one kind of electricity, say positive electricity, to pass round the circuit. In going round the circuit in the Daniell cell, starting with the zinc, the different junctions are met with in the order



and this is a very convenient method of representing the Daniell or any other cell.

Now at the junction $Zn/ZnSO_4$ positive electricity tends to pass from zinc to solution at a potential (pressure) of 0·52 volts, as indicated by the arrow. Further, as the osmotic pressure of $Cu\cdot$ ions in copper sulphate solution is greater than the solution pressure of copper, positive electricity tends to pass across the junction $CuSO_4/Cu$, in the direction of the arrow at an E.M.F. of 0·585 volts. It is clear that the forces at the two poles are in the same direction, and therefore positive electricity tends to pass through the solution in the direction indicated by the lower arrow at a total E.M.F. of

$$0{\cdot}520 + 0{\cdot}585 = 1{\cdot}105 \text{ volts.}$$

Further illustrations are given at a later stage.

Influence of Change of Concentration of Salt Solution on the E.M.F. of a Cell—The general equation just given may be written in a slightly different form by substituting for the pressures the corresponding concentrations. Considering first the solution pressure, P_1, of the zinc, it is theoretically possible to choose a $Zn\cdot\cdot$ ion concentration, C_1, such that its osmotic pressure will just balance the solution pressure of the metal; this may be substituted for P_1 in the general equation. Similarly, for p_1, the osmotic pressure of the zinc ions in the solution, we may substitute the corresponding concentration, c_1. Dealing in the same way with the copper side of the cell, the equation for the Daniell cell (or any other cell of similar type) becomes

$$E = E_1 - E_2 = \frac{0{\cdot}058}{n}\left(\log_{10}\frac{C_1}{c_1} - \log_{10}\frac{C_2}{c_2}\right).$$

In this form the general equation may be employed to investigate the question as to how the E.M.F. of the cell is affected by varying the concentration of the salt solutions. For the zinc side, since C_1 is greater than c_1, it is clear that the quotient C_1/c_1, and therefore E_1, is *increased* by diminishing c_1, the concentration of the $Zn\cdot\cdot$ ions. For the copper side, however, as C_2 is less than c_2 (p. 360), the quotient C_2/c_2, therefore E_2, will evidently be *diminished* by diminishing the

copper sulphate concentration. The general rule with regard to the influence of change of ionic concentration on the E.M.F. of a cell may be expressed as follows: *Diminishing the concentration of a solution from which ions are separating lowers, and diminishing the concentration of a solution into which new ions are going increases, the E.M.F. of a cell.* It is evident from general principles that the effect must be as described; in the first case, the tendency to the separation of ions is lessened, and the E.M.F. falls; in the second case, the entrance of new ions is facilitated, and the E.M.F. increases.

If the concentration of the $Cu^{\cdot\cdot}$ ions in the solution is progressively diminished, a point must be reached at which the solution pressure of the metal is just balanced by the osmotic pressure of the $Cu^{\cdot\cdot}$ ions. If the concentration is still further diminished, the tendency for copper to pass into solution will steadily increase, and ultimately may become greater than the tendency of zinc to pass into solution. It should therefore be theoretically possible to reverse the direction of the current in the Daniell cell by sufficiently diminishing the $Cu^{\cdot\cdot}$ ion concentration, and this state of affairs can be realized *experimentally* by adding potassium cyanide to the copper sulphate solution.

A further important deduction can also be drawn from the general equation. As c_1 and c_2 stand for the concentration of the positive *ions* in the solution, the E.M.F. of the cell should be independent of the nature of the negative ion, provided that the salts are equally ionized. This consequence of the theory is completely borne out by experiment. For twenty-one different thallium salts, in N/50 solution, the difference of potential between metal and solution varied only from 0·7040 to 0·7055 volts, the slight variations being readily accounted for by differences in the degree of ionization.

Concentration Cells—We have now to consider what are termed "concentration cells," cells in which the E.M.F. depends essentially on differences of concentration. In some respects, concentration cells are simpler than those of the Daniell type, which have so far been considered.

Concentration cells may be divided into two main classes:—

(*a*) Those in which the *solutions* (and therefore the active ions) are of different concentrations.
(*b*) Those in which the *electrode materials yielding the ions* are of different concentrations.

(*a*) **Concentration Cells with Solutions of Different Concentrations**—As a type of the elements in question, we will consider a cell in which silver electrodes dip in solutions of silver nitrate of different concentrations, c_1 and c_2. The arrangement for the practical determination of the total E.M.F. of such a combination is shown in Fig. 44, where A and B represent the cells containing the silver nitrate solutions and the

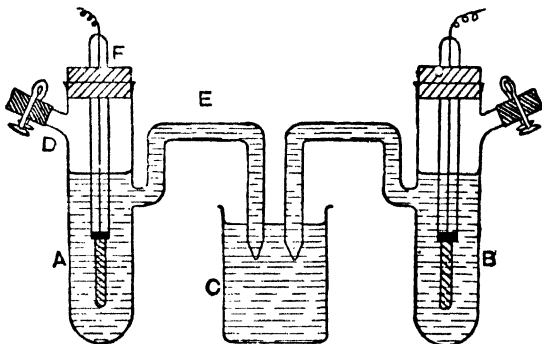


FIG. 44.

vessel C contains an indifferent electrolyte. As this form of cell is largely employed in measurements of E.M.F., it may be well to describe it fully. It consists of a glass tube 3-4 cm. wide, with a straight side-tube, D, on one side and a bent side-tube, E, on the other, the latter being employed for making connection with the indifferent electrolyte in C as shown. Into the lower end of a glass tube, F, is cemented a thick rod of silver covered with the finely-divided metal by electrolysis, and the glass tube is held by a cork closing the cell. The cell is filled with a solution of silver nitrate of definite strength through the bent tube by suction through the straight side-tube, D, which is then closed by a clip. The other "half-cell," B, is prepared in exactly the same way, but contains a solution of silver nitrate

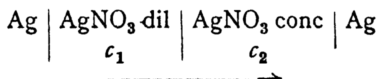
of different concentration. The ends of the bent tubes are then dipped into an indifferent electrolyte in the vessel, C, as shown, and the total E.M.F. of the combination determined by the potentiometer method in the usual way, connection with the silver electrodes being made by wires passing down the interior of the glass tubes. In this case, the general equation for an electrolytic cell,

$$E = \frac{0{\cdot}058}{n}\left(\log_{10}\frac{C_1}{c_1} - \log_{10}\frac{C_2}{c_2}\right)$$

simplifies to

$$E = \frac{0{\cdot}058}{n}\left(\log_{10}\frac{c_2}{c_1}\right) \quad . \quad . \quad . \quad (1)$$

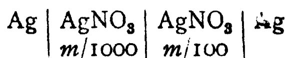
since C, the solution pressure of the metal, is the same on both sides, and is therefore eliminated. A cell of the type



works in such a way that silver is deposited from the more concentrated solution, in which the osmotic pressure is higher, and is dissolved at the pole in contact with the weaker solution, which offers less resistance to the entrance of Ag· ions. The change, therefore, proceeds in such a way that the differences of concentration tend to equalize, and when the solutions have reached the same concentration, the current stops. Positive electricity therefore passes *in the element* from the weak to the strong solution, as indicated by the arrow, and *in the connecting wire* from the strong to the weak solution; the electrode in contact with the strong solution becomes positively charged, the other electrode negatively charged.

The equation shows that the E.M.F. of such a concentration cell depends only on the respective concentrations of the positive ions in the two solutions and their valency, and not on the nature of the electrodes or on the nature of the anions, and the experimental results are in full accord with this deduction. Otherwise expressed, the E.M.F. of any element made up of a univalent metal, M, dipping in solutions of one of its salts of different concentration is of the same absolute value as that of

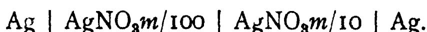
the silver concentration cell, provided that the solutions are of corresponding concentration, and ionized to the same extent. Further, if the solutions are dilute, and electrolytic dissociation therefore fairly complete, the ratio of the ionic concentrations in different dilutions will be approximately the same as the ratio of the concentrations themselves. Thus, in the example under consideration, the ratio c_2/c_1 for 1/100 molar, and 1/1000 molar solutions, will be approximately 10 : 1 ; $\log_{10} c_2/c_1$ is therefore 1, and the value of E for the cell



$$Ag \mid \begin{matrix} AgNO_3 \\ m/1000 \end{matrix} \mid \begin{matrix} AgNO_3 \\ m/100 \end{matrix} \mid Ag$$

is $0{\cdot}058/n = 0{\cdot}058$ volts, since n, the valency of the ions concerned, is unity.

If, however, the solutions are more concentrated, the fact that ionization is incomplete must be taken into account in calculating the E.M.F. of a cell. Suppose, for instance, it is required to calculate the E.M.F. of the cell



$$Ag \mid AgNO_3 m/100 \mid AgNO_3 m/10 \mid Ag.$$

N/10 silver nitrate solution is ionized to the extent of 82 per cent. at 18°, whence $c_2 = 0{\cdot}082$, and N/100 silver nitrate to the extent of 94 per cent., whence $c_1 = 0{\cdot}0094$. We have therefore $c_2/c_1 = 0{\cdot}082/0{\cdot}0094 = 8{\cdot}72$, and $E = 0{\cdot}054$ volts, in excellent agreement with the experimental value.

Strictly speaking, it is not justifiable in cells of this type to neglect the contact difference of potential between the two solutions, which may amount to a considerable fraction of the total E.M.F. The accurate formula for the calculation of the E.M.F. of cells of this type is given in a succeeding section (p. 382). If, however, both solutions contain an indifferent electrolyte in equivalent concentration great in comparison with those of the active salt, the difference of potential at the liquid junction becomes negligible, and the above formula (1) holds accurately (*cf.* p. 382).

It is evident from the formula that the E.M.F. of a concentration cell cannot be greatly altered by increasing the concentration on one side, owing to the limited solubility of the salts used as electrolytes. On the other hand, the E.M.F.

may be greatly altered by diminishing the ionic concentration on one side. Conversely, when a cell is made up with a solution of silver nitrate of known Ag· ion concentration, c_1, and one of unknown concentration, c_o, and the E.M.F. of the cell is measured, c_o can readily be calculated. This principle has been applied more particularly for the determination of very small ion concentrations, and may be illustrated by the determination of the Ag· ion concentration in a saturated solution of silver iodide. When the concentration on one side is very small, it is usual to add some salt, with or without a common ion, to eliminate the potential difference at the liquid junction, and also to increase the conductivity in the cell, so as to render the measurements more accurate. In this case potassium nitrate may conveniently be used. The observed E.M.F. of the cell



$$Ag \mid KNO_3 + AgI \mid AgNO_3\ 0{\cdot}001m + KNO_3 \mid Ag$$

is 0·22 volts. Since $c_1 = 0{\cdot}001$, we have

$$E = 0{\cdot}22 = 0{\cdot}058 \log_{10} (0{\cdot}001/c_o),$$

whence $c_o = 1{\cdot}6 \times 10^{-8}$. In other words, a litre of a saturated solution of silver iodide contains $1{\cdot}6 \times 10^{-8}$ mol of silver iodide, in excellent agreement with the value, $1{\cdot}5 \times 10^{-8}$ mol, obtained from conductivity measurements (p. 306).

(*b*) **Cells with Different Concentrations of the Electrode Materials (Substances Producing Ions)**—Not only can concentration cells be obtained by employing different concentrations of an electrolyte, but also by using different concentrations of metals or other electrode materials yielding ions. The concentration of metals can for our present purpose be most satisfactorily varied by employing their solutions in mercury, the so-called amalgams. For example, a concentration cell can readily be built up as follows :—

Zinc amalgam conc./zinc sulphate solution/zinc amalgam dilute



which differs from the cells of the first type in that the osmotic pressure of the zinc ions in contact with the two poles is the same, but the concentration, and therefore the solution pressure of the metal on the two sides, is different.

The E.M.F. of a cell of this type is represented by the general formula (p. 361)

$$E = \frac{0{\cdot}0001983\,T}{n}\left(\log_{10}\frac{P_1}{p_1} - \log_{10}\frac{P_2}{p_2}\right).$$

Since the same solution (in this case zinc sulphate) is in contact with both electrodes, $p_1 = p_2$, and the formula becomes

$$E = \frac{0{\cdot}0001983\,T}{n}\log_{10}\frac{P_1}{P_2}.$$

On the assumption that P_1 and P_2, the solution pressure of the zinc in the concentrated and dilute amalgams respectively, are proportional to the respective concentrations, we obtain

$$E = \frac{0{\cdot}0001983\,T}{n}\log_{10}\frac{C_1}{C_2}$$

which is exactly the same form of equation as that for cells with different electrolyte concentrations.

As the solution pressure of the zinc is higher in the concentrated amalgam, it passes into solution from the latter and is deposited in the less concentrated amalgam, so that the concentrations tend to become equal. It follows that positive electricity passes *in the cell* from the concentrated to the dilute amalgam, as shown by the arrow.

As an illustration, the E.M.F. of a cell for which $C_1 = 0{\cdot}14$ mol and $C_2 = 0{\cdot}00214$ mol of zinc per litre of amalgam at 23° may be calculated. If it be assumed that zinc is unimolecular when dissolved in mercury, $n = 2$, and

$$E = \frac{0{\cdot}0001983 \times 296}{2}\log_{10}\frac{0{\cdot}14}{0{\cdot}00214} = 0{\cdot}053 \text{ volts},$$

in excellent agreement with the observed value, 0·052 volts.

So far, the possible effect of mercury on the potential has been disregarded, and this is justified by the excellent agreement between observed and calculated values for the E.M.F. on the assumption that mercury simply acts as an indifferent solvent. The explanation is that for a mixture of two metals it is the metal with the higher solution pressure that goes into solution,

and mercury can consequently be used as solvent in potential measurements for any metal which is "less noble," *i.e.*, which has a higher solution pressure than mercury itself.

As indicated above, the E.M.F. of a metal dissolved in mercury depends on the concentration. The difference of potential between a saturated solution of a metal in mercury and an aqueous solution of one of its salts is the same as that between the salt solution and the pure metal, and even for dilute amalgams the E.M.F. is not very different from that of the pure metal, as the example shows. On the other hand, the potential of a metal in chemical combination with a more noble metal may be quite different from that of the pure metal.

The energy relations in concentration cells in which very dilute solutions are employed are remarkable. In the silver nitrate concentration cell described above, the change consisted simply in bringing Ag ions from the pressure p_1 to the lower pressure p_2. When a perfect gas expands from the pressure p_1 to p_2, no *internal* work is done, and this is the more nearly the case for ordinary gases the lower the pressures. In an exactly corresponding way no internal work will be done when a salt is further diluted in sufficiently dilute solution; in other words, the heat of dilution will be zero. This means that the change of chemical energy (Q in the Helmholtz formula), also termed the heat of reaction, is zero, so that *the electrical energy obtained from a concentration cell with sufficiently dilute solutions does not come from a chemical change at all, but entirely from the surroundings.* Under these circumstances, as Q is zero, the Helmholtz formula simplifies to

$$E = T\frac{dE}{dT}.$$

Electrodes of the First and Second Kind. The Calomel Electrode—So far only electrodes which are reversible with regard to the positive ion have been considered; these are termed *electrodes of the first kind.* In an exactly similar way it is possible to construct electrodes which are reversible with regard to the negative ion—these are termed *electrodes of the second kind.* They are prepared by immersing a metal in a saturated solution of one of its difficultly soluble salts, which

solution also contains a salt with the same anion as the insoluble salt. The E.M.F. of the electrode depends only on the concentration of the anion, since the concentration of all the other substances is constant. The most important electrode of this type is the calomel electrode, which consists of mercury in contact with solid mercurous chloride and a saturated solution of the latter salt in potassium chloride solution as electrolyte. The calomel electrode is reversible with regard to Cl′ ions, just as the $Cu/CuSO_4$ electrode is reversible with regard to Cu·· ions. If positive electricity passes from metal to solution, the mercury combines with Cl′ ions and calomel is formed; if passed in the reverse direction chlorine goes into solution and solid calomel disappears. The electrode, therefore, acts like a plate of solid chlorine, which gives up or absorbs the element depending on the direction of the current.

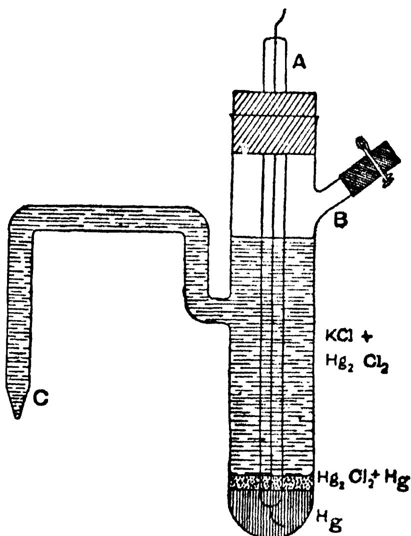


FIG. 45.

As the tendency of Cl′ ions to enter or leave the solution depends on the concentration of Cl′ ions already present, the difference of potential between mercury and the solution must depend on the concentration of the potassium chloride solution used, as already pointed out. A normal solution is mostly largely employed.

The calomel electrode is largely used as a *normal electrode* by means of which the E.M.F.'s of other electrodes may be compared; its chief advantage for this purpose is that it can readily be reproduced with an accuracy of about 1 millivolt. A convenient form of the electrode is shown in Fig. 45. A vessel

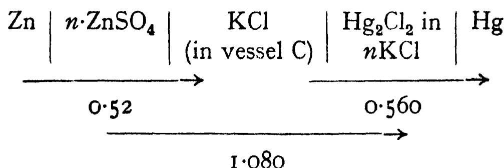
of the type already described in connection with concentration cells (p. 367) may conveniently be used. A layer of dry mercury is first placed in the bottom of the vessel, then a paste made by rubbing in a mortar mercury and calomel with some of the potassium chloride solution, and the vessel is then filled up with *n*-potassium chloride solution which has previously been saturated with calomel by shaking with excess of the latter. Connection with the mercury may conveniently be made by means of a platinum wire sealed at the bottom into a glass tube, A, the latter passing up through the rubber stopper closing the vessel. In making measurements, the bent side-tube, C, must also be filled with the potassium chloride solution. This is done by suction at the straight side-tube, B, which is then closed by a clip.

For measuring the potential of another electrode by means of the calomel electrode, the arrangement already shown in Fig. 44 is used.

Neglecting for the present the differences of potential at the liquid junctions, the E.M.F. of the combination in question is the algebraic sum of the differences of potential at the two metal/solution junctions. It follows that if the single potential difference between mercury and solution is known, the single potential difference at the other electrode can readily be calculated. Unfortunately no single potential difference is known with certainty (see next section), and it is, therefore, necessary to refer them to an arbitrary standard. Two such standards are in general use, (*a*) the so-called "absolute" standard; (*b*) the hydrogen standard. As regards the first standard, Ostwald assumes that the potential difference between mercury and the solution in the normal calomel electrode is 0·560 volts at 18°, the mercury being positive, and differences of potential referred to this standard are termed "absolute potentials," ϵ_c (see next section). On the other hand, Nernst refers E.M.F.s to the hydrogen standard, ϵ_h, the difference of potential between a platinum electrode saturated with hydrogen and a solution of an acid normal with regard to H· ions being put equal to zero. The "absolute" potentials, referred to the calomel electrode, have a theoretical basis, and there is reason to suppose that the real, but at present unknown, single potential differences

are not very different from the "absolute" potentials. Independently of this, however, the use of the calomel electrode in actual measurements is justified by the fact that it can be reproduced with a high degree of accuracy. The use of the hydrogen electrode as standard is purely arbitrary, as it is not pretended that the difference of potential between electrode and solution is actually zero, but the reference of potential differences to this standard has certain advantages. It is, in fact, usual to make the actual measurements with the calomel electrode, and then to refer them to the hydrogen standard, on the basis that when the hydrogen electrode is taken as zero the E.M.F. of the normal calomel electrode is + 0·283 volts; that of the electrode with N/10KCl + 0·336 volts, at 18°.

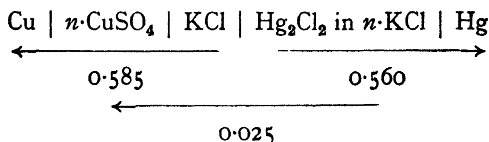
In order to illustrate the use of the calomel electrode for potential measurements, the separate determination of the differences of potential metal/solution for the two parts of the Daniell cell will be considered. When the zinc electrode is combined with the calomel electrode, as shown in Fig. 44, to form the cell



the E.M.F. of the combination, as shown by potentiometer measurements, is 1·080 volts, the zinc being negative with regard to mercury, so that positive electricity flows in the cell from zinc to mercury, as indicated by the lower arrow. In order to obtain the potential difference $Zn/ZnSO_4$, we proceed as follows (p. 364): It is known that mercury in contact with a solution of calomel becomes positively charged, and that for the calomel electrode the tendency for positive electricity to pass across the junction towards the mercury is 0·560 volts. The tendency for positive electricity to pass round the circuit is equivalent to 1·080 volts, hence the E.M.F. at the $Zn/ZnSO_4$ junction must act in the direction shown by the upper left-hand arrow, and is 1·080 — 0·560 = 0·52 volts. In other words, the

E.M.F. at the junction $Zn/ZnSO_4$ is 0·520 volts, the zinc being negatively charged.

Similarly, the observed E.M.F. of the cell



is 0·025 volts, the copper being positive with regard to mercury, hence positive electricity flows from mercury to copper in the cell, as indicated by the lower arrow. As far as the calomel junction is concerned, the tendency for positive electricity to flow round the circuit is equivalent to 0·560 volts towards the right, as indicated by the arrow. Hence in order that for the whole cell the tendency of positive electricity may be to flow towards the left at a potential of 0·025 volts the E.M.F. at the $Cu/CuSO_4$ junction must act in the opposite direction to that at the calomel junction and exceed it by 0·025 volts. The E.M.F. at the junction $Cu/CuSO_4$ is therefore 0·585 volts and positive electricity flows from solution to copper, as indicated by the arrow.

The total E.M.F. of the cell $Zn/ZnSO_4/CuSO_4/Cu$ is, therefore, $- 0{\cdot}520 + (- 0{\cdot}585) = - 1{\cdot}105$ volts, which agrees with the value obtained by direct measurement (p. 350). It is evident from the above that although the single potential differences at the junctions depend upon the value of the potential assumed for the standard, the E.M.F. of the complete cell does not depend upon the E.M.F. of the standard, which is eliminated.

If referred to the hydrogen electrode as standard, the potential difference $Zn/n{\cdot}ZnSO_4$ is $- 0{\cdot}520 + (- 0{\cdot}283) = - 0{\cdot}803$ volts, and that for $Cu/n{\cdot}CuSO_4$ is $+ 0{\cdot}585 + (- 0{\cdot}283) = + 0{\cdot}302$ volts, the E.M.F. of the Daniell cell being as before $= (- 0{\cdot}803) + (- 0{\cdot}302) = - 1{\cdot}105$ volts.

As reference electrodes for alkaline solutions, the mercuric oxide electrodes Hg/HgO in n.NaOH and Hg/HgO in n/10NaOH are most convenient. The same kind of vessel may be used as for the calomel electrode. The potentials, which become

constant after 2-3 days, are for the normal electrode $E_h = +0{\cdot}114$ volt and for the N/10 electrode $+ 0{\cdot}169$ volt at 18°.

As reference electrode for acid solutions the hydrogen electrode (p. 374) or the mercurous sulphate electrode Hg/Hg_2SO_4 in $n.H_2SO_4$ may be used. For the latter $\epsilon_h = + 0{\cdot}689$ volt at 18°.

Single Potential Differences. The Capillary Electrometer—When mercury and sulphuric acid are in contact in a capillary tube, and the arrangement is connected with a source of E.M.F. in such a way that the mercury is in contact with the negative pole and the acid with the positive pole, the area of the surface of separation between acid and mercury tends to diminish. The following out of this observation of Lippman's has led to an approximate estimate of the absolute differences of potential at metal/solution junctions.

When mercury and sulphuric acid have been in contact for some time, it is probable that there is a constant difference of potential between them, brought about in a rather complicated way. We have already learnt that well-defined differences of potential are established when a metal is in contact with a solution of one of its salts of definite concentration, and that is probably the state of affairs in the present case. We may suppose that some of the mercury dissolves in the sulphuric acid to form mercurous sulphate, and that the solution immediately in contact with the mercury is saturated with regard to the salt. As, however, the osmotic pressure of solutions of mercury salts is in general greater than the solution pressure of mercury, $Hg_2^{\cdot\cdot}$ ions deposit on the mercury and the latter becomes positively charged with regard to the solution. The two kinds of electricity attract each other, and we will assume with Helmholtz that the effect of this attraction is that there is a layer of positive electricity near the surface of the mercury holding a corresponding layer of negative electricity near the surface of the acid (" Helmholtz double layer ") (*cf.* Fig. 42).

Now there will be a certain surface-tension at the junction mercury/solution in the capillary tube, and, as is well known, the effect of surface tension is to make the areas of the surfaces in contact as small as possible. This tendency will, however, be counteracted by the electric layers; the positive charges

will repel each other and tend to enlarge the surface, and the same is true of the negative charges. The effect of the difference of potential is, therefore, to diminish the surface tension. The fact that a contrary E.M.F. applied to the junction tends to diminish the surface of separation between acid and mercury will now be readily understood. The contrary E.M.F. diminishes the difference of potential between acid and mercury, part of the force diminishing the surface tension is removed, and the latter attains more nearly its true value when undisturbed by electrical forces. When the contrary E.M.F. is gradually increased, the surface tension increases at first, attains a maximum value, beyond which it gradually diminishes. It is plausible to suppose that the surface tension increases as the difference of potential between mercury and acid gets smaller and smaller, that it attains its maximum value when the contact E.M.F. at the junction is just neutralized by the contrary E.M.F., and that it again diminishes as the latter is further increased and the surfaces become charged with electricity of opposite sign to the original charges. This at once gives us a method of determining single differences of potential. It is only necessary to note when the surface tension attains its maximum value; under these circumstances the applied E.M.F. is clearly equal to the single difference of potential at the junction mercury/solution and the problem as to the value of a single potential difference is solved. In this way Ostwald estimated the E.M.F. of the normal calomel electrode at 0·560 volts.

Unfortunately the matter is not quite so simple as the above considerations would lead us to suppose, and it is fairly certain that the absolute potentials arrived at in this way may differ to some extent from the true values. It has already been pointed out that two standards are in use, and that the use of the calomel electrode for measuring differences of potential has certain practical advantages.

Before considering another method which has been suggested for measuring single differences of potential, it should be mentioned that the phenomena just described have been utilized in the construction of an electrometer—the so-called *capillary electrometer*—which, as already mentioned (p. 357),

can be used as a null instrument in E.M.F. measurements by the compensation method. A convenient form of the capillary electrometer is represented in Fig. 46. A tube, C, 4·5 mm. internal diameter and a bulb-tube, A, are connected by a vertical capillary tube, B, 0·5 mm. internal diameter. So much mercury is poured into C that it stands at a convenient height in the capillary tube. A quantity of mercury is also placed in A, and the latter and the capillary are then filled up with dilute sulphuric acid. As indicated in the figure the two quantities of mercury can be connected with the positive and negative poles of a source of E.M.F. when required.

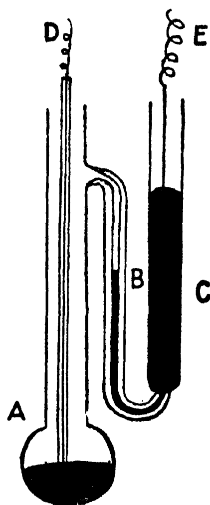


Fig. 46.

The wire, D, connected with the mercury in the bulb-tube is sealed in a glass tube so as not to come in contact with the sulphuric acid. When the apparatus is so arranged that the mercury and acid are in equilibrium at a point in the capillary tube and the two quantities of mercury are then connected with a source of E.M.F. the potential at the junction in the capillary tube will alter owing to alteration in the concentration of mercurous salt produced by the current. The surface tension between acid and mercury must therefore also change (p. 377) and also the position of the junction in the capillary, since the position of the meniscus depends to some extent on the surface tension between mercury and acid.

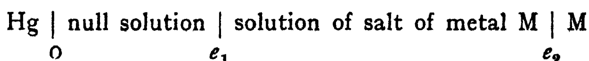
The use of the apparatus as an electrometer will now be evident. It is best so to arrange matters that the mercury at the narrow surface is connected with the negative pole of the external source of E.M.F. through a tapping key, and the junction is observed through a small microscope. If an external E.M.F. is applied, the surface will move when the key is momentarily depressed, and for small differences of potential (up to 0·01 volt) the movement of the meniscus is proportional to the applied

E.M.F., so that the name electrometer is justified. When the applied E.M.F. is zero, no movement of the meniscus occurs on making contact, and the electrometer may therefore be used as a null instrument. When not in use, the electrometer should be connected up with a cell of E.M.F. not exceeding 1 volt.

An alternative very instructive method of determining single potential differences, the theory of which is due mainly to Nernst and the practical realization to Palmaer, will now be described. When mercury in a fine stream is allowed to flow into an electrolyte containing a definite concentration of mercurous salt (*e.g.*, mercurous chloride), $Hg_2^{\cdot\cdot}$ ions from the solution deposit on the drops as they enter (the osmotic pressure of $Hg_2^{\cdot\cdot}$ ions in the solution being greater than the solution pressure of the mercury), the drops thus become positively charged, and further become surrounded with a layer of the liberated Cl' ions. When the drops reach the bottom of the vessel containing the electrolyte, the positive ions are given up and reunite with the Cl' ions to form more calomel. The net result of this process is that the solution gets poorer in calomel where the drops enter, and richer where they unite with the mercury. A concentration cell is thus formed, and it is evident that positive electricity must flow from the weak to the strong solution, that is, from top to bottom of the vessel, a deduction which is borne out by experiment.

Now it must be possible to reduce the concentration of $Hg_2^{\cdot\cdot}$ ions to such a point that the osmotic pressure of the $Hg_2^{\cdot\cdot}$ ions is just equal to the solution pressure of the mercury; there is then no deposition of $Hg_2^{\cdot\cdot}$ ions on the entering drops, and no current flows. *Conversely, when no current results when mercury is dropped into an electrolyte containing $Hg_2^{\cdot\cdot}$ ions, the difference of potential between mercury and the solution must be zero.* If the $Hg_2^{\cdot\cdot}$ ion concentration is still further reduced, the solution pressure of the mercury is greater than its osmotic pressure in the solution, and the current flows in the opposite direction.

The $Hg_2^{\cdot\cdot}$ ion concentration was reduced by adding potassium cyanide till the point of no current and therefore zero difference of potential was reached. The solution in equilibrium with mercury under these conditions may be termed the null solution. If then a cell is built up of the type



e_2, the difference of potential between metal and solution, can be determined directly if the E.M.F. e_1 at the junction of the solution is known or can be made negligible.

In this way Palmaer has found that the E.M.F. at the junction Hg/n/10KCl saturated with Hg_2Cl_2 is 0·573 volts at 18°, corresponding with about − 0·520 volts for n/1KCl, as compared with Ostwald's value of 0·560 volts.

Some writers consider that the problem of the determination of single potential differences is thus finally settled, but Palmaer himself does not consider that all the difficulties of the measurements have been overcome, so that the above results should only be taken as provisional.[1]

Potential Differences at Junction of Two Liquids—Up to the present, we have left out of account the possible differences of potential at the junction of two solutions. When the E.M.F. of a cell is considerable, the error thus arising is only slight, but if the E.M.F. is small, as for many concentration cells, the potential difference at the liquid contact becomes of importance.

It has been shown by Nernst that in many cases these differences of potential can be calculated according to his theory of electromotive force, and the results obtained in this way have been fully confirmed by experiment. The calculation is effected most readily for solutions of the same electrolyte in different concentrations, for example, solutions of hydrochloric acid. When the solutions are brought in contact the acid will tend to diffuse from the more concentrated to the more dilute solution. As, however, the acid is highly ionized, the H· and Cl′ ions will diffuse independently, and, as the former move the more rapidly, the dilute solution will soon contain an excess of H· ions and the strong solution an excess of Cl′ ions. Owing to the electric charges conveyed by the moving ions, the dilute solution will become positively charged, and the strong solution negatively charged. However, the excess of positive electricity in the dilute solution will retard the entrance

[1] *Cf.* Palmaer, *Zeitsch. physikal. Chem.*, 1907, **59**, 129.

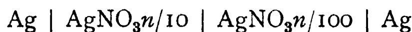
of H· ions and accelerate the Cl′ ions, so that in a short time the ions will be moving at the same rate. The difference of potential thus produced will persist until both solutions attain the same concentration. The above considerations show that *the contact difference of potential between two solutions is due to the different migration velocities of the two ions, and the dilute solution takes the potential corresponding with that of the more rapid ion.* The contact difference of potential between different solutions of the same salt will be the smaller the more nearly the speed of the two ions agrees, and this explains why solutions of potassium chloride and of ammonium nitrate are used as connecting solutions in potential measurements (compare p. 369).

It can easily be shown that the potential difference, E, between two solutions of a binary electrolyte with univalent ions (for example, hydrochloric acid) is represented by the formula

$$E = \frac{u - v}{u + v} \frac{2 \cdot 3026 \, RT}{F} \log_{10} \frac{c_1}{c_2}$$

where c_1 and c_2 represent the ionic concentrations of the two solutions, and u and v the migration velocities of the anion and cation respectively. From the above equation it can be calculated that the contact E.M.F. between N/10 and N/100 hydrochloric acid is 0·036 volt, a result which is fully confirmed by experiment.

From the above result, the value of E may be calculated for the cell



$$Ag \mid AgNO_3 n/10 \mid AgNO_3 n/100 \mid Ag$$

when the contact difference of potential between the two solutions is not practically eliminated by the use of potassium nitrate. Taking the junctions in order, we have

$$E = \frac{2 \cdot 3026}{F}\left[RT \log_{10} \frac{C_1}{c_1} + \frac{u - v}{u + v} RT \log_{10} \frac{c_1}{c_2} - RT \log_{10} \frac{C_2}{c_2}\right]$$

$$= \frac{2 \cdot 3026}{F}\left[\frac{u - v}{u + v} RT \log_{10} \frac{c_1}{c_2} - \frac{u + v}{u + v} RT \log_{10} \frac{c_1}{c_2}\right]$$

$$= - \frac{v}{u + v} \cdot 2 \times 0 \cdot 058 \log_{10} \frac{c_1}{c_2}$$

for room temperature.

For silver nitrate $\frac{v}{u + v} = 0{\cdot}522$ (p. 255), $c_1 = 0{\cdot}082$, $c_2 = 0{\cdot}0094$.

Hence

$$E = 0{\cdot}522 \times 2 \times 0{\cdot}058 \times 0{\cdot}945 = 0{\cdot}057 \text{ volts},$$

in excellent agreement with the value found experimentally, 0·055 volts.

Gas Cells—So far we have dealt only with solid substances and amalgams as electrode materials, but it is interesting to note that gases may be used in the same way. This is made possible by using metallic electrodes, usually of platinum coated with the finely-divided metal, as absorbents for the gases. The prepared platinum electrode is partially immersed in a solution of an electrolyte containing ions derived from the gas, and the gas is bubbled through till the potential difference between electrode and solution becomes constant.

As an example of a gas electrode, the hydrogen electrode already referred to, will be described. The form of cell represented in Fig. 44 may be used; it is half-filled with normal acid, the platinum pole, held by a well-fitting cork, is partially immersed in the acid, and hydrogen gas is passed in by the bent side-tube and allowed to bubble through the acid for ten or fifteen minutes till the electrode is saturated. The straight side-tube, which has been open, is now closed by a clip, and the electrode is ready for use. The platinum pole itself usually consists of a piece of platinum foil joined by hammering to a platinum wire, the latter being sealed into the bottom of the glass tube carried by the cork closing the cell. Electrical connection may be made by a copper wire passing down through the glass tube and dipping into a little mercury at the bottom, the mercury being also in contact with the upper part of the platinum wire which projects into the interior of the glass tube.

The electrode is completely reversible and behaves like a plate of metallic hydrogen. When positive electricity passes from solution to metal, hydrogen ions are discharged according to the equation $2H^{\cdot} \rightarrow H_2$; when it goes in the contrary direction gaseous hydrogen becomes ionized according to the converse equation, $H_2 \rightarrow 2H^{\cdot}$.

A hydrogen concentration cell is obtained when two hydrogen

electrodes, containing the gas at different pressures, are combined in the usual way. Such cells correspond exactly with those made up with amalgams of different concentrations. The direction of the current is such that the pressures on the two sides tend to become equal, so that hydrogen becomes ionized at the high pressure side and is discharged as gas at the low pressure side.

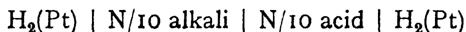
In calculating the E.M.F.s of such cells by the general formula (p. 371) it has to be remembered that, since the hydrogen molecule contains two atoms, the work gained in bringing a mol of the gas reversibly from the pressure P_1 to the lower pressure P_2 is RT $\log_e P_1/P_2$, whilst if the same change is carried out electrically, $H_2 + 2F \rightarrow 2H^{\cdot}$, the energy concerned is 2FE coulombs. Hence, since $2FE = RT \log_e P_1/P_2$ the E.M.F. of the cell is

$$E = \frac{RT}{2F} \log_e \frac{P_1}{P_2}.$$

The same formula applies to gas cells in which chlorine and other diatomic gases are used (see also p. 394). On the other hand, since 4F coulombs are associated with the solution of 1 mol of oxygen ($O_2 + 2H_2O - 4F \rightleftarrows 4OH'$) the E.M.F. of an oxygen concentration cell is

$$E = \frac{RT}{4F} \log_e \frac{P_1}{P_2}.$$

Another type of hydrogen concentration cell is obtained when the gas concentration in the electrodes is constant and the $H^{\cdot}$ concentration in contact with the two electrodes is different. An interesting cell of this type is built up as follows :—


H_2(Pt) | N/10 alkali | N/10 acid | H_2(Pt)

Since the equilibrium $H + OH' \rightleftarrows H_2O$ always holds, there must be a minute concentration of $H^{\cdot}$ even in alkaline solution and therefore the above represents a hydrogen concentration cell. From the E.M.F. of the above cell which, after applying a correction for the contact difference of potential, amounts to 0·6951 volt at 18°, the product of the ionic concentration

for water, $[H^\cdot][OH'] = K_w$ can be calculated as follows. From the general equation $E = 0{\cdot}0577 \log_{10} c_1/c_2$ we have

$$0{\cdot}6951 = 0{\cdot}0577 \log_{10} c_1/c_2$$

c_1, the $H^\cdot$ concentration in N/10 acid at 18°, is 0·0888, hence

$$c_1/c_2 = 0{\cdot}0888/c_2 = 10^{12{\cdot}045}$$

and c_2, the $H^\cdot$ concentration in N/10 alkali $= 0{\cdot}0888 \times 10^{-12{\cdot}045}$. The OH' concentration in the same solution, allowing for incomplete dissociation, is 0·0892. Therefore

$$[H^\cdot] \times [OH'] = 0{\cdot}0888 \times 10^{-12{\cdot}045} \times 0{\cdot}0892 = 0{\cdot}7 \times 10^{-14}$$

at 18°, which is in excellent agreement with the value found by other methods (p. 298).

Cells in which the electrodes are in contact with *different* gases, for example, the hydrogen-oxygen cell, are referred to below.

Potential Series of the Elements—During the consideration of the Daniell cell (p. 362), it was pointed out that metals differ greatly with regard to their solution pressures. Zinc, for example, has a very high solution pressure, whilst that of copper is very small.

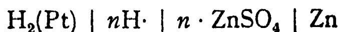
The difference of potential between a metal and a solution of one of its salts at room temperature is represented by the formula

$$E = \frac{0{\cdot}058}{n} \log_{10} \frac{P}{p},$$

and if p, the osmotic pressure of the positive ions of the salt, is the same for all the electrodes, say that represented by a solution containing a gram-ion per litre, it is evident that the value of E is proportional to the solution pressure of the metal. As regards the standard to which the E.M.F.s are to be referred, the hydrogen standard has in this case certain advantages. The potential of metals with regard to normal-ionic solutions of their salts is therefore obtained by measuring the E.M.F. of cells of the type

$H_2(Pt)$ | $nH^{\cdot}$ | normal ionic solution of the metallic salt | metal, the difference of potential $H_2(Pt)$ | $nH^{\cdot}$ being taken as zero.

The E.M.F. of the combination

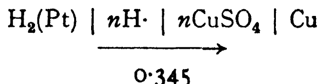


$$H_2(Pt) \mid nH^{\cdot} \mid n \cdot ZnSO_4 \mid Zn$$

$$0{\cdot}760$$

measured with the potentiometer in the usual way, is 0·760 volts, the hydrogen being positive with regard to the zinc. The value of E_{ZnSO_4-Zn} is therefore $+$ 0·760 volts, the potential difference at the other junction being zero by definition, and positive electricity goes in the cell in the direction indicated by the arrow, that is, the *solution tension of zinc is greater than that of hydrogen, so that the former displaces the latter* (*indirectly*) *from solution.*

On the other hand, the E.M.F. of the cell



$$H_2(Pt) \mid nH^{\cdot} \mid nCuSO_4 \mid Cu$$

$$\xrightarrow{\hspace{3em}}$$

$$0{\cdot}345$$

is 0·345 volts, copper being positive; positive electricity goes in the solution in the direction represented by the arrow. Hydrogen therefore goes into solution and copper is deposited, so that the solution pressure of hydrogen is *greater* than that of copper.

The numbers obtained as above indicated, that is the difference of potential between a metal and a normal-ionic solution of one of its salts (solutions which contain a gram of the corresponding ion per litre) are termed the *normal potentials* or *electrolytic potentials* of the metals in question and are usually indicated by the symbol ϵ_0. In a similar way the normal potentials of electrodes which yield negative ions (such as oxygen, chlorine, and bromine) may be measured.

The following table contains the normal potentials ϵ_{oh} for a large number of elements referred to the hydrogen electrode as standard. The normal potentials referred to the normal calomel electrode, ϵ_{oc} (its potential being taken as zero), are obtained from the normal hydrogen potentials by means of the formula $\epsilon_{oh} = \epsilon_{oc} + 0{\cdot}283$ volts.

The numbers for chlorine, bromine, and iodine, are comparable with the others, and are obtained in a somewhat similar way. The value for chlorine, for example, may be obtained by measuring the E.M.F. of a cell of the type.



$$H_2(Pt) \mid n \cdot H^{\cdot} \mid n \cdot Cl' \mid Cl_2(Pt),$$

the right-hand electrode being reversible for chlorine just as the left-hand one is reversible for hydrogen (see below).

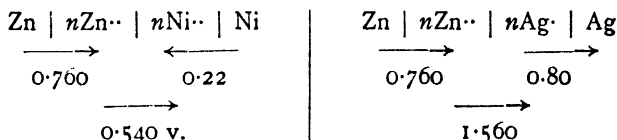
Normal Potentials, ϵ_{oh}.

Na	Mg	Al	Mn	Zn	Fe	Cd
− 2·7	− 1·55	− 1·34	− 1·07	− 0·76	− 0·44	− 0·40

Tl	Co	Ni	Sn/Sn··	Pb	H_2	Cu
− 0·34	− 0·29	− 0·22	− 0·14	− 0·13	± 0	+ 0·345

Hg/Hg_2··	Hg/Hg··	Ag	Pt	Au/Au···	O	I	Br	Cl	F
0·80	0·86	0·80	0·86	1·3	1·2	0·54	1·08	1·40	1·9

By means of this table, the E.M.F. of a cell made up of two metals in contact with normal solutions of their salts can at once be calculated. As the following schemes show, a zinc-nickel element has the E.M.F. 0·760 − 0·22 = 0·540 volts, and a zinc-silver element the E.M.F. 0·760 − (− 0·80) = 1·560 volts.



positive electricity flowing in the respective cells, in the directions indicated by the lower arrows. The student should have no difficulty in understanding these schemes in the light of the considerations advanced on page 364. Both in the case of zinc and of nickel the solution pressure of the metal is greater than the osmotic pressure of the metallic ions in normal solution, and, therefore, when arranged to form a cell, the tendency for positive electricity to pass round the circuit is in the opposite direction at the two junctions. Positive electricity, therefore, flows

in the direction in which the acting force is the greater, and the total E.M.F. is the *difference* of the forces at the two junctions. In the zinc-silver cell, on the other hand, the forces act in the same direction, and the total E.M.F. is therefore the *sum* of the forces at the junctions.

According to Nernst's formula, and in agreement with the convention now widely used that the potential difference has the positive sign if the electrode is positively charged with respect to the solution and the negative sign if the electrode is negatively charged, the normal potential is represented by the formula

$$\epsilon_0 = -\frac{RT}{nF}\log_e C$$

since c, the concentration of the ions, in the above measurements is unity. Therefore the general formula representing the P.D. between an electrode and an electrolyte of the ionic concentration c is

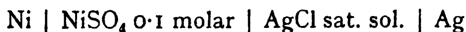
$$E = -\frac{RT}{nF}\log_e \frac{C}{c} = \epsilon_0 + \frac{RT}{nF}\log_e c$$

when the electrode gives positive ions, and

$$E = \epsilon_0 - \frac{RT}{nF}\log_e c$$

when the electrode gives negative ions.

In order to illustrate the use of these formulæ we may calculate the P.D. at each electrode and the total E.M.F. of the cell


Ni | $NiSO_4$ 0·1 molar | AgCl sat. sol. | Ag

at 25°, assuming that the P.D. at the liquid contact is eliminated and that the nickel salt is 60 per cent. ionized. [ϵ_0 for nickel − 0·22 volts; ϵ_0' for silver 0·80 volts.]

The formula is as follows :—

$$E = \epsilon_0 + \frac{RT}{n_1F}\log_e c_1 - \epsilon_0' - \frac{RT}{n_2F}\log_e c_2$$

n_1 for nickel is 2 and c_1 is 0·06; n_2 for silver is 1 and c_2 is $1{\cdot}25 \times 10^{-5}$ gram-ions per litre at 25°. Hence

$$E = -0{\cdot}25 + 0{\cdot}029 \log_{10}(0{\cdot}06) - 0{\cdot}80 - 0{\cdot}058 \log_{10}(1{\cdot}25 \times 10^{-6})$$
$$- 0{\cdot}22 - 0{\cdot}035 - 0{\cdot}80 + 0{\cdot}289$$
$$= -0{\cdot}766.$$

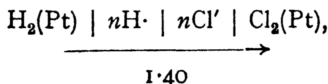
The total E.M.F. of the cell is − 0·766 volts; the P.D. at the silver electrode is + 0·511 volts, and at the nickel electrode − 0·22 − ·035 = − 0·255 volts.

In order to avoid errors of sign, it is well to check results such as the above from the point of view of general principles. Since diminishing the concentration of a solution from which ions are separating lowers, and diminishing the concentration of a solution into which new ions are going increases the E.M.F. at a junction (p. 366), it is evident that the effect on the E.M.F. of alteration of the concentrations of the solutions must be as shown above.

From the above considerations it would appear that metals which stand higher than hydrogen in the tension series can liberate hydrogen from acids and that the numbers in the table afford an approximate measure of the energy of the change. On the other hand, hydrogen at atmospheric pressure should displace the metals which stand below it in the tension series. This has been shown to hold in some cases at least with hydrogen occluded in platinized platinum electrodes, the platinum presumably acting as a catalyst for reactions which under ordinary conditions are extremely slow. Finally each metal should be able to displace from combination any metal below it in the tension series, the difference of potential between the metals being a measure of the free energy of the change. On the whole these conclusions are borne out by the experimental results except in so far as the phenomenon of over-voltage comes into play. This subject is briefly discussed in a later section (p. 399).

Cells with Different Gases—The simplest example of these cells is the hydrogen-chlorine cell, already referred to. One-half of the cell consists of a hydrogen electrode in acid, the other of a similar electrode saturated with chlorine, and the two electrodes are combined as represented in Fig. 44, the intermediate vessel containing acid of the same strength as that in the cell. The chemical change which takes place in the cell

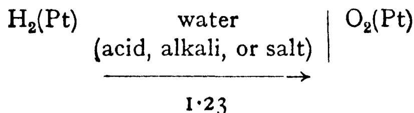
is the combination of hydrogen and chlorine to form hydrochloric acid. Representing the cell as usual



$$H_2(Pt) \mid nH^{\cdot} \mid nCl' \mid Cl_2(Pt), \quad \xrightarrow[1{\cdot}40]{}$$

it is clear that positive electricity flows in the cell from hydrogen to chlorine in the direction represented by the arrow, the chlorine becoming the positive and the hydrogen the negative pole. The E.M.F. of the cell in normal acid at the ordinary temperature is about 1·40 volts.

The most important cell of this type is the hydrogen-oxygen or Grove's cell, the two poles being saturated with hydrogen and oxygen respectively. When connection is made the gases gradually disappear, hydrogen becoming ionized at one pole and oxygen uniting with water to form hydroxyl ions at the other pole. The cell may therefore be represented by the following scheme :—



$$H_2(Pt) \quad \text{water (acid, alkali, or salt)} \mid O_2(Pt) \quad \xrightarrow[1{\cdot}23]{}$$

and positive electricity flows through the cell from hydrogen to oxygen as represented by the arrow, so that hydrogen is the negative pole and oxygen the positive pole. The hydrogen electrode is reversible with regard to hydrogen, as follows: $H_2 \rightleftarrows 2H^{\cdot}$, the reaction taking place at the oxygen electrode is as follows: $H_2O + \frac{1}{2}O_2 \rightleftarrows 2OH'$. When employed as indicated above, the change is that represented by the two upper arrows and 2F passes through the wire; when, on the other hand, 2F is sent through the cell in the opposite direction, the changes at the two poles are represented by the two lower arrows.

If absolutely indifferent electrodes were used for absorbing the gases, and the changes at the electrodes were fully reversible, the calculated E.M.F. of the cell is 1·23 volts.[1] The

[1] Corresponding with the free energy of formation of water from its elements. The calculation is rather complicated. (Compare Nernst and von Wartenberg, *Zeitsch. physikal. Chem.*, 1906, **56**, 544.)

values actually observed are smaller, probably owing to the formation of an oxide of platinum, which has an oxygen potential different from that of free oxygen.

Theoretically, only pure water is necessary as electrolyte, but, in order to increase the conductivity, dilute acid or alkali or a dilute salt solution is employed as electrolyte. The E.M.F. of the cell is independent of the nature of the electrolyte since the product $[H^{\cdot}][OH']$ is the same in acid, alkaline, or neutral salt solution, but this is not the case for the single potential differences at the electrodes.

Oxidation-Reduction Cells—The gas cell just described is a typical oxidation-reduction cell, as when working hydrogen is being oxidized at the negative pole and oxygen reduced at the positive pole.

As may be anticipated, corresponding cells can be constructed in which instead of hydrogen another reducing agent is used, and instead of gaseous oxygen another oxidizing agent. Indifferent metals, such as platinum or iridium, are used as electrodes in all cases.

We will first consider a cell built up of a hydrogen electrode on one side and a platinized platinum electrode dipping in a solution of a *ferrous* and a *ferric* salt on the other. When the two electrodes are connected up, a current flows *in the cell* from the hydrogen to the other electrode. Hence at the hydrogen electrode gaseous hydrogen is going into solution as hydrogen ions according to the equation $H_2 + 2F = 2H^{\cdot}$,[1] and at the other electrode $Fe^{\cdot\cdot\cdot}$ ions are being reduced to $Fe^{\cdot\cdot}$ ions according to the equation $2Fe^{\cdot\cdot\cdot} - 2F = 2Fe^{\cdot\cdot}$, the charges neutralizing each other through the wire and thus producing a current. When the same quantity of electricity is passed through the cell in the opposite direction, $Fe^{\cdot\cdot}$ ions are converted to $Fe^{\cdot\cdot\cdot}$ ions, and hydrogen gas is liberated at the other pole; the cell therefore works reversibly, and the measurement of the E.M.F. gives a measure of the free energy or affinity of the reaction. The total change is, of course, expressed by the equation $2Fe^{\cdot\cdot\cdot} + H_2 = 2Fe^{\cdot\cdot} + 2H^{\cdot}$.

Other oxidizing agents can be measured in the same way against the hydrogen electrode, and from the results a table

[1] 2F or 2 × 96,500 coulombs converts a mol of hydrogen to H ions.

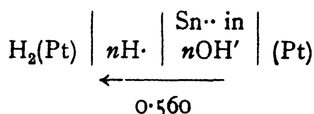
of various solutions, arranged in the order of their oxidizing potentials, can be obtained. Some of the values obtained in this way may be given :—

$SnCl_2$ in HCl	0·23 volts	$FeCl_3$ in HCl	0·98 volts
NH_2OH in HCl	0·38 volts	$KMnO_4$ in H_2SO_4	1·50 volts

The above are only meant to indicate the order of the results, as the accurate values depend greatly on the concentration and composition of the solutions.

The four solutions mentioned, even stannous chloride, in acid solution exert an oxidizing action on gaseous hydrogen, and therefore the direction of the current is the same as in the ferric chloride cell. As might be anticipated, potassium permanganate has the highest oxidation potential.

When, on the other hand, a platinum electrode dipping into a solution of stannous chloride in potassium hydroxide is connected with a hydrogen electrode so as to form a cell

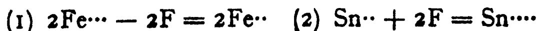


hydrogen ions are discharged and the stannous salt becomes oxidized, positive electricity, therefore, flowing in the cell in the direction of the arrow. The change which takes place in the cell may be represented by the equation $2H^{\cdot}+Sn^{\cdot\cdot}=Sn^{\cdot\cdot\cdot\cdot}+H_2$, the hydrogen acting as the oxidizing agent. In this case we may say that the stannous chloride solution has a certain reduction potential.

The above considerations are sufficient to show that the terms "oxidizing agent" and "reducing agent" are *relative* and not *absolute*; whether a substance acts as an oxidizing or a reducing agent depends on the substance with which it is brought in contact.

The hydrogen electrode may be replaced by a platinum electrode dipping in a solution of a reducing agent, an oxidation-reduction cell containing only liquids being obtained. One well-known cell of this type consists of platinum electrodes

dipping in solutions of ferric chloride and stannous chloride respectively. The changes at the electrodes may be represented by the equations



$$(1)\ 2Fe^{\cdots} - 2F = 2Fe^{\cdot\cdot} \quad (2)\ Sn^{\cdot\cdot} + 2F = Sn^{\cdot\cdot\cdot\cdot}$$

and the total change as follows :—



$$2Fe^{\cdots} + Sn^{\cdot\cdot} = 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}$$

It is now easy to understand what at first sight appears very puzzling, that a ferric salt can oxidize a stannous salt at a distance, the solutions being in separate cells and possibly connected by an indifferent solution. The above equations show that the essential feature of the phenomenon is the transference of two positive charges from the iron to the tin ions through the wire.

As a definite potential may be ascribed to every substance acting as an oxidizing or reducing agent, it is clear that the E.M.F. of an oxidation-reduction cell may be represented as the algebraic sum of the differences of potential at the two junctions. When a strong oxidizing solution is combined with a still stronger oxidizing solution to form a cell, the former will be oxidized at the expense of the latter, but the E.M.F. of the cell will be small, as the solutions are acting against each other. The further apart two solutions are in the oxidation-reduction potential series, the greater will be the E.M.F. of the cell formed by their combination.

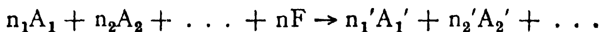
We are now in a position to give a clear definition of oxidation and reduction in dilute salt solutions. *An increase in the number of positive charges or a diminution in the number of negative charges on an ion denotes oxidation ; decrease in the number of positive charges or increase in the number of negative charges on an ion denotes reduction.* The usual definition of oxidation as consisting in an addition of oxygen to a compound or the abstraction of hydrogen from it, is clearly inapplicable to salt solutions, but the older definition retains its value for changes in which organic compounds are concerned, and for solid compounds ; these have so far been very little investigated from an electro-chemical standpoint.

According to the above definition all reactions which take

place electromotively are oxidation-reduction reactions, oxidation taking place at one electrode and reduction at the other. In the Daniell cell, for instance, oxidation takes place at the cathode, $Zn + 2F \rightarrow Zn^{\cdot\cdot}$, and reduction at the anode $Cu^{\cdot\cdot} - 2F = Cu$. It follows that the displacement of one metal by another is to be regarded as an oxidation-reduction process. Elements which can only give positively charged ions, *e.g.*, the typical metals, can only act as reducing agents, whilst elements such as chlorine, which only yield negatively charged ions, invariably exert an oxidizing action. Solutions, on the other hand, may behave according to the conditions either as oxidizing or reducing agents, since one or the other ion may react. Cupric bromide solution, for instance, acts as an oxidizing agent towards zinc and as a reducing agent towards copper. Moreover, a single ion, *e.g.*, ferrous ion, $Fe^{\cdot\cdot}$ may act either as an oxidizing or as a reducing agent since it can be changed into uncharged Fe or into $Fe^{\cdot\cdot\cdot}$.

Electromotive Force and Chemical Equilibrium—In the previous section, we have considered oxidation-reduction cells from the qualitative standpoint only. Just as in the case of the Daniell cell, which indeed is a special type of oxidation-reduction cell, the E.M.F. at an electrode depends upon the concentration of all the ions taking part in the change. Thus the E.M.F. at a platinized platinum electrode immersed in a solution of a ferric salt is only definite when a certain proportion of $Fe^{\cdot\cdot}$ ions are also present, and the E.M.F. depends on the concentrations of both ferric and ferrous salt. The general equation representing the dependence of the E.M.F. of such cells on the concentrations of the substances taking part in the reaction will now be given.

The reversible reaction $n_1A_1 + n_2A_2 + \ldots \rightleftarrows n_1'A_1' + n_2'A_2' \ldots$ (p. 166), when it proceeds in one direction in an electrolytic cell, may be represented by the equation



$$n_1A_1 + n_2A_2 + \ldots + nF \rightarrow n_1'A_1' + n_2'A_2' + \ldots$$

which indicates that n_1 mols of A_1 and n_2 mols of A_2 . . . are converted into n_1' mols of A_1' and n_2' mols of A_2' by taking up n faradays. The maximum work obtainable when the substances on one side of the equation at definite concentrations

are transformed isothermally and reversibly into the substances on the other side of the equation also in definite concentrations may be derived by a non-electrical method or by carrying out the reaction in a galvanic cell. In the former case the maximum work may be stated in the form

$$A = RT\left(\log_e K - \log_e \frac{[A_1']^{n_1'}[A_2']^{n_2'}}{[A_1]^{n_1}[A_2]^{n_2}}\right)$$

where the square brackets represent concentrations and K represents the equilibrium constant. When the process is carried out in a galvanic cell the maximum work obtained is $A = nFE$ (p. 353) hence

$$E = \frac{RT}{nF}\left(\log_e K - \log_e \frac{[A_1']^{n_1'}[A_2']^{n_2'}}{[A_1]^{n_1}[A_2]^{n_2}}\right).$$

When both the initial substances and the final products are in unit concentration the maximum work obtainable non-electrically is

$$A = RT \log_e K$$

and in a galvanic cell $nF\epsilon_0$, where ϵ_0 is the normal potential. Hence the general equation representing the dependence of the E.M.F. of the cell on the concentrations of the reacting substances is

$$E = \epsilon_0 - \frac{RT}{nF}\log_e \frac{[A_1']^{n_1'}[A_2']^{n_2'}}{[A_1]^{n_1}[A_2]^{n_2}}.$$

The concentrations of the more highly oxidized substances (*i.e.*, those formed by taking up positive charges) occur in the denominator.

For the change



$$Fe^{\cdot\cdot} + F \rightleftarrows Fe^{\cdot\cdot\cdot}$$

the above expression has the form

$$E = \epsilon_0 - \frac{RT}{F}\log_e [Fe^{\cdot\cdot}]/[Fe^{\cdot\cdot\cdot}].$$

For the chlorine electrode $2Cl' + 2F \rightleftarrows Cl_2$

$$E = \epsilon_0 - \frac{RT}{2F}\log_e [Cl']^2/[Cl_2].$$

As regards the permanganate electrode, for which the equation $MnO_4' + 8H^{\cdot} - 5F \rightleftarrows Mn^{\cdot\cdot} + 4H_2O$ represents the probable chemical change, the expression for the E.M.F. is as follows :—

$$E = \epsilon_0 - \frac{RT}{5F} \log_e \frac{[Mn]^{\cdot\cdot} [H_2O]^4}{[MnO_4]' [H^{\cdot}]^8}.$$

It is clear from the above equations that the effect on the E.M.F. of the cell of systematic variation in the concentrations of the reacting substances throw light on the nature of the chemical change taking place in the cell and also on the number of faradays associated with the change in question.

Electrolysis and Polarization—If an external E.M.F. of 1 volt is applied to two platinum electrodes dipping in a concentrated solution of hydrochloric acid, it will be found that the large current which at first passes when connection is made rapidly diminishes and finally falls practically to zero. The explanation of this behaviour is that while the current is passing hydrogen accumulates on the cathode and chlorine on the anode, thus setting up an E.M.F. which acts against the E.M.F. applied to the poles of the cell. This phenomenon is termed *polarization.* In the above case the gases go on accumulating in the electrodes till the back E.M.F., which we will term *e*, is equal to the applied E.M.F., when the current ceases. If, however, an E.M.F. of 1·5 volts is applied at the electrodes, a continuous current passes through the solution and it is evident that in this case the back E.M.F. *e* has not attained the value of 1·5 volts. The explanation is evident when it is remembered that the E.M.F. of a cell in which platinum electrodes are charged with hydrogen and chlorine respectively at atmospheric pressure is 1·40 volts (p. 390). When an E.M.F. of 1·5 volts is applied, the electrodes become charged up to atmospheric pressure, but no higher, the excess of the gases escaping into the atmosphere. It follows that *e* cannot under ordinary circumstances attain a higher value than 1·40 volts, so that electrolysis proceeds at an E.M.F. of $E - e = 0{\cdot}10$ volts.

The E.M.F. which must just be exceeded in order that a continuous current may pass through an electrolyte is termed the "*decomposition potential*" of the electrolyte, and it is clear from the above example that *the decomposition potential is equal*

to the E.M.F. of a cell in which the products of electrolysis are the combining substances. As the E.M.F. of such a cell is the algebraic sum of the differences of potential at the electrodes, it is clear that the decomposition potential is also the sum of two factors, namely, the sum of the potentials required to discharge the anion and cation respectively.

The decomposition potential of an electrolyte may be determined in two ways. According to the first method, the external E.M.F. applied to the electrodes is gradually raised and the point noted at which there is a sudden increase in the current. The value of the current, C, is determined by the equation

$$E - e = CR,$$

where R is the resistance of the circuit, and will obviously increase rapidly as soon as E is greater than e. The second method is to charge the electrodes up to atmospheric pressure by using an E.M.F. greater than e, then the external circuit is broken and the E.M.F. of polarization measured at once. This method depends upon the fact already indicated, that the decomposition potential is that E.M.F. which is just sufficient to overcome the E.M.F. of polarization.

As has just been pointed out, the potential required to discharge an ion such as $Zn^{\cdot\cdot}$ must just exceed the difference of potential at the junction $Zn/Zn^{\cdot\cdot}$, and is, therefore, the same as the potential of the metal in volts in the tension series (p. 387). Further, the E.M.F. required to decompose an electrolyte is clearly the sum of the separate differences of potential required to discharge the anion and cation respectively, and is, therefore, obtained by adding the values for the two ions in the tension series. The matter becomes clearer when we consider that the potential difference between an element and its ions may conveniently be regarded as a measure of the affinity of the element for electricity. Thus the affinity of zinc for positive electricity is equivalent to 0·760 volts, and that of chlorine for negative electricity to 1·40 volts. To convert zinc ions to metallic zinc we must, therefore, apply a contrary E.M.F. which just exceeds the affinity of zinc for positive electricity, in other words, the decomposition potential of zinc ions is 0·760 volts.

On this basis, the decomposition potential of zinc chloride

should be 0·760 + 1·40 = 2·070 volts, of hydrochloric acid 1·40 volts, and of copper chloride (− 0·345 + 1·40) = 1·055 volts respectively. This is fully confirmed by the experimental determinations of Le Blanc, who obtained the following values: $ZnCl_2$ = 2·15 volts, HCl = 1·31 volts, $CuCl_2$ = 1·05 volts, an agreement within the limits of experimental error.

Separation of Ions (particularly Metals) by Electrolysis— The results just mentioned are well illustrated by the phenomena observed when a *mixture* of electrolytes is electrolized at different values of the applied E.M.F. The foregoing considerations show that on gradually raising the E.M.F. that chemical change takes place most readily for which the least difference of potential is required, and this may be taken advantage of for the electrolytic separation of metals which are discharged at different potentials. Suppose, for example, a mixture of hydrochloric acid, zinc and copper chlorides is subjected to electrolysis. Below 1 volt practically no change will occur, but at 1·1 volts, a little above the decomposition potential for copper chloride, copper will be deposited on the cathode. When it has been almost completely removed, and the potential is raised to 1·4 volts, hydrogen will be liberated at the cathode. Finally, the attempt may be made to remove zinc by raising the external E.M.F. above 2·2 volts, but this cannot be effected in acid solution, as there is a large excess of hydrogen ions, which are more easily discharged than zinc.

In an exactly corresponding way, almost all the bromine may be electrolytically separated from a solution containing zinc chloride and zinc bromide before the chlorine appears.

It is, therefore, clear that it is the value of the E.M.F., and not the strength of the current, which is of primary importance for the separation of metals, and in recent years methods based on this principle have become of great commercial importance. Besides the value of the applied E.M.F., the concentration of the ions in contact with the cathode is of great importance, as the decomposition potential necessarily depends on the ionic concentration, and hence great attention is now paid to the efficient stirring of the electrolyte.[1]

[1] The electrolytic separation of metals on this principle is described in recent papers by Sand (*Journal of the Chemical Society*, 1907, **91**, 373, 1908, **93**, 1572), and others.

The Electrolysis of Water. Overvoltage (Supertension) at Electrodes—When aqueous solutions of many salts and strong acids and bases are electrolysed with smooth platinum electrodes only hydrogen and oxygen are liberated as products of electrolysis and the decomposition potential is in all cases about 1·66 volts. It was formerly supposed that one or both of these gases were formed by the action of the primary products of electrolysis on the solvent, but this does not account for the fact that the decomposition potential is in general the same for different acids and bases. It is now accepted, for reasons given below, that the gases are products of the primary decomposition of water.

If such is the case, and the decomposition of water proceeds reversibly at the electrodes, we would expect the decomposition potential to be about 1·2 volts, in agreement with the E.M.F. of the hydrogen-oxygen cell, whereas it is considerably higher. When, however, platinized platinum electrodes are used and the current is plotted against the applied E.M.F., the latter being gradually increased, it is found that there is a sudden increase in the current at 1·1 volts (so that water can be continuously decomposed at the latter potential), but a much more rapid increase at 1·66 volts. Two possible explanations of these remarkable facts might be suggested. Nernst was formerly of opinion that at the lower potential $H^{\cdot}$ and O'' ions are being discharged the current being very small because of the exceedingly minute concentration of the O'' ions. The more rapid decomposition at 1·66 volts is due to the discharge of $H^{\cdot}$ and OH' ions the latter combining to form water and oxygen according to the equation $4OH \rightarrow 2H_2O + O_2$.

Another mode of explaining the results is that the decomposition potential depends on the nature and condition of the electrode material; at many electrodes the potential must be raised above that theoretically required for reversible decomposition in order to reach the point of decomposition. Thus assuming that the decomposition of N/1 sulphuric acid takes place reversibly at a platinum cathode, the following values for the cathodic decomposition potential with other metals were obtained: Pd + 0·26, Pt ± 0, Fe − 0·03, Cu − 0·19, Al − 0·27, Pb − 0·36, Hg − 0·44. Thus hydrogen is eliminated

more easily at a palladium than at a platinum electrode, perhaps owing to the formation of an alloy with the former metal; in all other cases a greater or less excess of E.M.F. is required in order to liberate the gas. Overvoltage phenomena also occur at the anode when oxygen is being liberated, but in this case the order of the metals is not the same as with hydrogen. The magnitude of the overvoltage increases considerably with increase of current-density.

There is no doubt as to the great importance of overvoltage phenomena, although they are not yet fully understood. They appear to depend, in part at least, on supersaturation with the gas. Thus when hydrogen is liberated at a platinized platinum anode, the latter dissolves a large amount of the gas and facilitates its escape in bubbles, thus bringing about equilibrium between the gas in solution and in the gas space. On the other hand smooth platinum, and such metals as lead and mercury, have very little solvent power for hydrogen, and a much higher pressure is required in order to force in sufficient of the gas to admit of the formation of bubbles (Nernst). According to Förster, the liberated substance forms some compound with the electrode material, and the supertension is determined by the concentration of the gas thus dissolved in some form in the electrode. By making use of the high concentration of hydrogen obtainable at electrodes showing considerable supertension, reductions not readily effected by other methods can be performed.

Supertension phenomena have an important bearing on the dissolving of metals in acids. Pure zinc should liberate hydrogen from acids at a potential of 0·770 volts but the supertension is so great as almost to reach this value and the reaction therefore proceeds very slowly. The overvoltage at impure zinc is much less and therefore the metal dissolves much more readily in acids. In the latter case local differences of potential doubtless also play a part.

The main evidence in favour of the view that water undergoes primary decomposition during electrolysis is that the decomposition potential is largely independent of the electrolyte, whether acid, base, or salt; and further, that of the possible changes which can take place at the electrodes the decomposi-

tion of water is usually that which can take place at the lowest potential (compare previous section). In the case of hydrochloric acid the relationships are more complicated. In concentrated solution the decomposition potential is lower than that of water (p. 398) and the main products are hydrogen and chlorine; with progressive dilution the decomposition potential rises and ultimately a mixture of oxygen and chlorine is liberated at the anode.

The decomposition potential curve of sulphuric acid shows two further points of rapid increase of current, at 1·95 and 2·0 volts respectively. It seems probable that the former value is connected with the discharge of SO_4'' and the latter with the discharge of HSO_4' ions.

Electrolysis and Polarization (*continued*)—The E.M.F. required to bring about decomposition of an electrolyte is not determined solely by the magnitude of the polarization due to the products of electrolysis. The current also causes concentration changes at the electrodes and these changes always act in opposition to the E.M.F. driving current through the cell. This effect is known as *concentration polarization* and is minimized by stirring the electrolyte.

Any substance which tends to diminish the polarization in a cell is termed a *depolarizor.* It may act as a catalyst in accelerating the changes at the electrodes, *e.g.*, platinized platinum in the liberation of hydrogen, or it may alter the change taking place at the electrodes to one that takes place more easily, *e.g.*, the use of potassium dichromate in the so-called bichromate cell. The " insoluble " salt in an electrode of the second kind acts as a depolarizer.

Recent investigations have shown that polarization occurs in many cases where it would not be anticipated, and this fact has raised the question as to the exact nature of the changes taking place at the electrodes during electrolysis. When, for instance, a current is passed through the cell Cu | $CuSO_4$ | Cu it would be anticipated according to the accepted views regarding electrolysis that $Cu^{\cdot\cdot}$ ions would be discharged at the cathode as metallic copper, that SO_4'' ions after discharge at the anode would immediately attach the latter forming copper

sulphate. As a matter of fact, Le Blanc[1] has shown that under these circumstances considerable polarization occurs both at anode and cathode, so that the changes taking place at the poles can scarcely be as simple as those just assumed. A still more striking case occurs in the electrolysis of solid silver salts between silver electrodes. With silver sulphate, for instance, a polarization E.M.F. of 0·312 volts was observed two minutes after breaking the circuit and at − 80° an E.M.F. of no less than 1·562 volts one minute after breaking the circuit.[2] The cause of these remarkable observations is still by no means understood.

Accumulators—As is well known, accumulators are employed for the storage of electrical energy. An accumulator is a reversible element; when a current is passed through it in one direction the electrodes become polarized, and when the polarizing E.M.F. is removed and the poles of the accumulator are connected by a wire, the products of electrolysis recombine with production of a current and the cell slowly returns to its original condition.

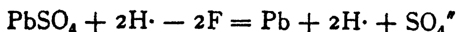
It will be clear from the above that the Grove's gas cell is a typical accumulator or secondary element; when a current is passed through it in one direction the electrodes become charged with hydrogen and oxygen, and these gases can be made to recombine with production of a current. From a technical point of view, however, a satisfactory accumulator must retain its strength unaltered for a long time when the poles are not connected, and must be easily transported. A gas accumulator would be in many respects unsuited for commercial purposes.

The apparatus most largely used for the storage of electricity is the *lead accumulator*, the electrodes of which in the uncharged condition contain a large amount of lead sulphate (obtained by the action of sulphuric acid on the *porous lead* of which the electrodes largely consist at first) and dip in dilute sulphuric acid. The accumulator is *charged* by sending an electric current through it. At the cathode, the lead sulphate

[1] M. le Blanc, *Abhandlungen der Bunsen-Gesellschaft*, No. 3, 1910.

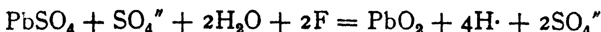
[2] Haber and Zawidzki, *Zeitsch. physikal. Chem.*, 1911, **78**, 228. Compare *Annual Reports Chemical Society for* 1912, p. 19

is reduced by the hydrogen ions (or rather by the discharged hydrogen) to metallic lead according to the equation



$$PbSO_4 + 2H^{\cdot} - 2F = Pb + 2H^{\cdot} + SO_4''$$

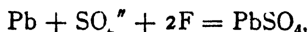
or more simply, $PbSO_4 - 2F = Pb + SO_4''$
On the other hand, the SO_4'' ions wander towards the anode and react with it according to the equation



$$PbSO_4 + SO_4'' + 2H_2O + 2F = PbO_2 + 4H^{\cdot} + 2SO_4''$$

so that the anode and cathode consist mainly of lead peroxide and metallic lead respectively.

On connecting up to obtain a current (discharging), SO_4'' ions are discharged at the *new* anode (the lead pole), and reconvert it to lead sulphate, according to the equation



$$Pb + SO_4'' + 2F = PbSO_4,$$

and simultaneously $H^{\cdot}$ ions are discharged at the *new* cathode (the peroxide pole), the peroxide being reduced to the oxide, and acted on by sulphuric acid to reform the sulphate, according to the equation



$$PbO_2 + 2H^{\cdot} + H_2SO_4 - 2F = PbSO_4 + 2H_2O.$$

The chemical changes taking place on charging and discharging are summarized in the equation



$$Pb + PbO_2 + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O\,;$$

the upper arrow represents discharging, and the lower arrow charging.

The E.M.F. of the lead accumulator is about 2 volts. It is not strictly reversible, but under ordinary conditions of working about 90 per cent. of the energy supplied and stored up in it can again be obtained in the form of work.

The only other accumulator of commercial importance is that developed more particularly by Edison and his co-workers, and known as the Edison accumulator. In the charged condition the positive plate consists of hydrated nickelic oxide,



$$Ni_2O_3,\ xH_2O$$

and the negative plate of finely divided iron, the electrolyte being about 4 N alkali. On discharging the nickelic oxide is reduced to nickelous hydroxide $Ni(OH)_2$ and the iron is oxidized to ferrous hydroxide $Fe(OH)_2$. According to Förster the changes taking place on charging and discharging are represented approximately by the equations

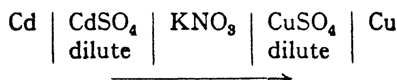


$$Fe + Ni_2O_3, 1{\cdot}2H_2O + 1{\cdot}8H_2O \rightleftarrows Fe(OH)_2 + Ni(OH)_2.$$

Both the anode and cathode consist of steel frames provided with a large number of pockets (made of nickel-plated steel) in which the active electrode materials are packed. The potential during discharge is about 1·34 volts, and, as the above equation shows, is independent (in practice only very slightly dependent) on the alkali concentration. One advantage possessed by the Edison accumulator is its comparative lightness.

Practical Illustrations. *Dependence of Direction of Current in Cell on Concentration of Electrolyte*—It has already been pointed out (p. 366) that the current in a Daniell cell may be reversed in direction by enormously reducing the $Cu^{\cdot\cdot}$ ion concentration by the addition of potassium cyanide. The two chief methods for diminishing ionic concentration are (1) the formation of complex ions (as in the above instance); (2) the formation of insoluble salts.

When a cell of the type



is set up, and the poles are connected through an electroscope, it will be found that positive electricity passes in the cell in the direction of the arrow. If some ammonium sulphide solution is then added to the copper sulphate solution, "insoluble" copper sulphide is formed, and the concentration of the $Cu^{\cdot\cdot}$ ions is reduced to such an extent that the current flows in the reverse direction.

If the Daniell cell



is built up in the same way, it will not be found possible to reverse the current by the addition of ammonium sulphide, owing to the greater solution pressure of the zinc as compared with cadmium; but if potassium cyanide is added, the current changes in direction, owing to the fact that the $Cu^{\cdot\cdot}$ ion concentration in a strong solution of potassium cyanide (in which the copper is mainly present in the complex anion $Cu(CN)_4''$) is considerably less than in a solution of copper sulphide.

The following experiments, which are described in considerable detail in the course of the chapter should if possible be performed by the student. For further details text-books on practical physical chemistry should be consulted.

(*a*) Preparation of a standard cadmium cell (p. 357).

(*b*) Measurement of the E.M.F. of a cell by the compensation method (p. 356).

(*c*) Preparation and use of a calomel "half-cell" (p. 373).

(*d*) Preparation and use of a capillary electrometer (p. 379).

(*e*) Measurement of the E.M.F. of a concentration cell (p. 367).

(*f*) Measurement of the E.M.F. of the hydrogen-oxygen cell (p. 390).

(*g*) Determination of the solubility of a difficultly soluble salt, *e.g.*, silver chloride, by E.M.F. measurements (p. 370).

PROBLEMS AND QUESTIONS

[Equilibrium Equations in Gaseous Systems: Dissociation]

(*cf.* problems 32-35)

The composition of a system can be expressed in various ways, and in representing the equilibrium conditions in a system in terms of an equilibrium constant the "constant" will differ according to the method used in expressing the composition. When the composition is expressed in terms of the relative concentrations of the components (preferably in mols per litre) the equilibrium equation, for a reaction represented by the general equation



$$n_1A_1 + n_2A_2 \ldots \rightleftarrows n_1'A_1' + n_2'A_2'$$

takes the form (p. 166)

$$\frac{[A_1]^{n_1}[A_2]^{n_2}\ldots}{[A_1']^{n_1'}[A_2']^{n_2'}\ldots} = K_c \qquad (1)$$

where the square brackets represent concentrations and K_c is the equilibrium constant.

When the composition is expressed in terms of the relative partial pressures of the components, the equilibrium equation takes the form

$$\frac{p_{A_1}^{n_1}p_{A_2}^{n_2}\ldots}{p_{A_1'}^{n_1'}p_{A_2'}^{n_2'}} = K_p \qquad (2)$$

where p_{A_1}, p_{A_2}, etc., are the respective partial pressures of the components and K_p is the equilibrium constant.

The relationship between K_c, the equilibrium constant, when concentrations are used, and K_p, the equilibrium constant for partial pressures can be obtained by means of the general gas equation

$$pv = nRT$$

in the form $p = cRT$ where $c = [A] = \frac{n}{v}$.

From equation (2) by substitution

$$K_p = \frac{[A_1]^{n_1}(RT)^{n_1}[A_2]^{n_2}(RT)^{n_2}\ldots}{[A_1']^{n_1'}(RT)^{n_1'}[A_2']^{n_2'}(RT)^{n_2'}\ldots}$$
$$= K_c(RT)^{\Sigma n}.$$

where $\qquad \Sigma n = n_1 + n_2 + \ldots - n_1' - n_2' -$

represents the alteration in the number of molecules during the reaction. R, the gas constant, has the value 0·0821 in litre-atmospheres.

These general results can be applied to the dissociation of gases such as phosphorus pentachloride and nitrogen dioxide. As in these cases $\Sigma n = 1$ we have

$$K_p = K_cRT$$

and as

$$K_p = \frac{x^2P}{1 - x^2}$$

(where P represents the total pressure)

$$K_c = \frac{x^2 P}{(1 - x^2)RT}.$$

This equation for K_c can be obtained from the alternative form given on p. 170, namely

$$K_c = \frac{x^2}{(1 - x)V}$$

by substituting for V its value in the equation

$$PV = (1 + x)RT.]$$

1. A certain quantity of a gas measures 100 c.c. at 25° and 700 mm. pressure. What pressure will be required to change the volume to 50 c.c. at − 10° C.? Ans. 1236 mm.

2. What volume is occupied by (*a*) 1 gram of nitrogen, (*b*) 1 gram of carbon dioxide at 20° and a pressure of 72 cm. of mercury?
Ans. (*a*) 906·3 c.c.; (*b*) 576·8 c.c.

3. An open vessel is heated till one-third of the air it contains at 20° is expelled. What is the temperature of the vessel? Ans. 117·6° C.

4. If 0·5 gram of a gas measure 65 c.c. at 10° and 500 mm. pressure, what is its molecular weight? Ans. 271·5.

5. If 1 gram of nitrogen, 1 gram of oxygen, and 0·2 gram of hydrogen are mixed in a volume of 2·24 litres at 0°, calculate the respective partial pressures of the gases in the mixture, in grams per sq. cm.
Ans. 369, 323, and 1025 grams/cm.^{2}

6. The density of benzyl alcohol, $C_6H_5CH_2OH$, at its boiling-point is 1·145. Compare the observed and calculated values of the molecular volume (p. 70). Ans. Obs. 123·7. Calc. 128·8.

7. The density of a solution containing 4·1375 grams of iodine in 100 grams of nitrobenzene is 1·2389 at 18°, the density of the solvent at the same temperature being 1·20547. From these data calculate the molecular solution volume of iodine. Ans. 67·2 c.c.

8. The density of formic acid at 20° is 1·2205 and n_D at the same temperature is 1·3717. Calculate the molecular refractivity of formic acid by the Lorentz formula and compare it with the value calculated from the atomic refractivities (*cf.* p. 75). Ans. Obs. 8·56. Calc. 8·35.

9. The value of n_D for a mixture of formic acid and water containing 62·7 per cent. of the latter was found to be 1·3625 at 19·5°, and the density at the same temperature 1·1462. Calculate the refraction constant by the Lorentz formula and compare it with that calculated on the assumption that the components exert their effects independently. [$D^{19°}$ for water 0·9984 N_D = 13333.] Ans. Obs. 0·1937. Calc. 0·1936.

10. Find the relationship between the solubility, *s*, of a gas and its absorption coefficient, *a*, in a liquid at *t*° (*cf.* p. 95).
Ans. $s/a = (273 + t°)/273$.

11. Calculate the gas constant, R, in litre-atmospheres from the observation that a solution containing 34·2 grams of cane sugar in 1 litre of water has an osmotic pressure of 2·522 atmospheres at 20°.
Ans. 0·0860.

12. The osmotic pressure of a 2 per cent. solution of acetone in water is equal to 590 cm. of mercury at 10°. What is the molecular weight of acetone? Ans. 60 (found), 58·0 (theor.).

13. What is the molecular concentration of an aqueous solution of urea which at 20° exerts an osmotic pressure of 4·6 atmospheres?
Ans. 0·19 molar.

14. The vapour pressure of ether (mol. wt. 74) is lowered from 38·30 cm. to 36·01 cm. by the addition of 11·346 grams of turpentine to 100 grams of ether. Calculate the molecular weight of turpentine.

Ans. 132 (theor. 138).

15. The vapour pressure of water at 50° is 92 mm. How much urea (mol. wt. 60) must be added to 100 grams of water to reduce the vapour pressure by 5 mm.? Ans. 18·1 grams.

16. A current of dry air was passed in succession through a bulb containing a solution of 30 cane sugar in 160 grams of water, through a bulb, at the same temperature, containing water, and finally through a tube containing concentrated sulphuric acid. The loss of weight in the water bulb was 0·0315 gram and the gain in weight in the sulphuric acid bulb 3·02 grams. Calculate the molecular weight of cane sugar in the solution.

Ans. 339.

17. The addition of 1·065 grams of iodine to 30·14 grams of ether raises the boiling-point of the latter by 0·296°. What is the molecular weight of iodine in ether? Ans. 251.

18. The vapour pressure of ether at 0° is 183·4 mm., at 20° 433·3 mm. Calculate the latent heat of vaporization per mol. of ether at 10°.

Ans. 6840 cal.

19. The vapour pressure of water over a mixture of $CuSO_4$, $5H_2O$ and $CuSO_4$, $3H_2O$ is 2·933 mm. at 13·95° and 21·701 mm. at 39·7°. Calculate the heat given out when 1 mol. of water combines with $CuSO_4$, $3H_2O$ to form $CuSO_4$, $5H_2O$. Ans. 13,730 cal.

20. 0·3 grams of camphor, $C_{10}H_{16}O$, added to 25·2 grams of chloroform raise the boiling-point of the solvent by 0·299°. Calculate the molecular elevation constant for chloroform. Ans. 38·2.

21. From the data in the previous question calculate the heat of vaporization per mol. of chloroform (boiling-point 61°). Ans. 6931 cal.

22. 1·2 grams of a substance dissolved in 24·5 grams of water (K = 18·5) caused a depression of the freezing-point of 1·05°. Find the molecular weight of the substance. Ans. 86.

23. Beckmann found that 0·0458 gram of benzoic acid in 15 grams of nitrobenzene (K = 80) caused a depression of the freezing-point of 0·099°. What conclusion can be drawn from this observation as to the molecular condition of benzoic acid in nitro benzene? Ans. Acid is associated.

24. At 343° the vapour pressure of ammonium bromide is 195 mm. and at 356° it is 289 mm. Calculate the heat of vaporization of ammonium bromide, assuming dissociation complete. Ans. 45,000 cal.

25. From formula (1), p. 140, deduce the expression

$$P = \frac{1000\ Hs}{24 \cdot 22} \cdot \frac{dT}{T} \text{ (p. 142)}$$

and hence calculate the osmotic pressure of an ethereal solution the boiling point of which is 35·2°. (Boiling-point of ether, 34·8°; latent heat of vaporization per gram, 84·5 cal.; $s = 0·70$.) Ans. 3·17 atmos.

26. At 21° the surface tension, γ, of diethyl sulphate in 28·28 dynes/cm.² and at 62·6° γ is 24·00 dynes/cm.² Find the value of c, the temperature coefficient of the molecular surface energy ($D^{21} = 1·0748$; $D^{62·6} = 1·0278$).

Ans. 2·17.

27. For monochlorhydrin γ at 17° is 47·61 dynes/cm.² (D = 1·3254) and at 57·8° 43·72 dynes/cm.² (D = 1·2883). What conclusions can be drawn from these data as to the molecular complexity of the liquid?

Ans. $c = 1·44$, liquid is associated.

28. Calculate the heats of formation of ethane, ethylene, and acetylene respectively from their elements at 17° (*a*) at constant pressure, (*b*) at constant volume from the following data. Heats of combustion: ethane 370,440 cal., ethylene 333,350 cal., acetylene 310,100 cal. Heats of formation: carbon dioxide 94,300 cal., liquid water 68,400 cal., all at constant pressure.

Ans. Ethane: C.P. 23,360 cal., C.V. 22,200 cal. Ethylene: C.P. − 7950 cal., C.V. − 8530 cal. Acetylene: C.P. − 53,100 cal., C.V. − 53,100 cal.

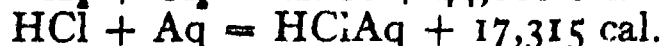
29. Find the heat of formation of anhydrous aluminium chloride from the following data (Thomsen):—



$$2Al + 6HClAq = 2AlCl_3Aq + 3H_2 + 239{,}760 \text{ cal.}$$



$$H_2 + Cl_2 = 2HCl + 44{,}000 \text{ cal.}$$



$$HCl + Aq = HClAq + 17{,}315 \text{ cal.}$$



$$AlCl_3 + Aq = AlCl_3Aq + 76{,}845 \text{ cal.}$$

Ans. 321,960 cal. (for Al_2Cl_6).

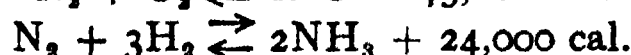
30. The heat of solution of anhydrous strontium chloride is 11,000 cal., that of the hexahydrate − 7300 cal. What is the heat of hydration of the anhydrous salt to hexahydrate. Ans. 18,300 cal.

31. The specific heats of diamond and graphite in the neighbourhood of 10° (0°-17°) are 0·1128 and 0·1604 calories per gram respectively. The heats of combustion are 94,310 and 94,810 calories per 12 grams respectively. Find the heat evolved in the transformation of graphite to diamond at 0° C. Ans. 490 cal.

32. In the synthesis of nitric acid and of ammonia the primary reactions are



$$N_2 + O_2 \rightleftarrows 2NO - 43{,}200 \text{ cal.}$$



$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 24{,}000 \text{ cal.}$$

Discuss fully the effect of temperature and pressure on these reactions and refer, for illustration, to the manufacturing processes; why is it that in these processes an elevated temperature is used, although one reaction is endothermic and the other exothermic?

At 2000° abs. $K = [NO]/[N_2]^{1/2}[O_2]^{1/2} = 0{\cdot}0153$.

Assuming the heat of reaction independent of temperature, calculate the equilibrium constant at 2500° abs. (*Birmingham Univ.*)

33. The vapour density of phosphorus pentachloride referred to air as unity was found to be 5·08 at 182°, 4·00 at 250°, and 3·65 at 300°, calculate the degrees of dissociation at these temperatures.

Ans. 41·7 per cent.; 80 per cent.; 97·3 per cent.

34. From the following data for the equilibrium $N_2O_4 \rightleftarrows 2NO_2$ at 49·7° calculate the degree of dissociation at each pressure and show, by finding the dissociation constant, that the law of mass action applies:—

Pressure in mm. Hg	26·80	93·75	182·69	261·37	497 75
Density (air = 1)	1·663	1·788	1·894	1·963	2·144

The vapour density of N_2O_4 is to be taken as 3·20 (air = 1).

Ans. 0·93; 0·789; 0·69; 0·63; 0·493.

35. Bodenstein found that the degree of dissociation of carbonyl chloride according to the equation $COCl_2 \rightleftarrows CO + Cl_2$, is 67 per cent. at 503°, 80 per cent. at 553°, and 91 per cent. at 603°. From these results calculate the heat of dissociation of carbonyl chloride.

Ans. 19,210 cal. from 503°-553°; 26,550 cal. from 553°-603°.

36. The ratio of distribution of aniline between benzene and water is 10·1 : 1. When a litre of aniline hydrochloride solution, containing 0·0997 mol. of the salt, was shaken with 59 c.c. of benzene at 25° it was found that 50 c.c. of benzene had taken up 0·0648 gram of aniline. Find the amount of hydrolysis of aniline hydrochloride in the solution and calculate the dissociation constant of aniline as a base (*cf.* p. 296).

Ans. 1·76 per cent., $3{\cdot}85 \times 10^{-10}$.

37. When heated in aqueous solution at 52·4° the concentration of sodium bromoacetate in solution was 11·0, 9·4, 7·9 and 6·9 at times 0, 26, 52, and 74 hours respectively from the commencement of the reaction, the decomposition being ultimately complete. Find the order of the reaction and calculate the times required to complete (*a*) one-third, (*b*) two-thirds of the change. Ans. Unimolecular. 65·2 hours, 177 hours.

38. In an experiment on the rate of reaction between sodium thiosulphate and ethyl bromoacetate (*cf.* p. 238) 50 c.c. of the reaction mixture required the following amounts of 0·0110 N iodine at the times from the commencement of the reaction indicated in the table.

t (min.)	0	5	10	15	25	40	∞
c.cs. iodine solution	37·25	24·7	18·75	15·3	11·6	8·85	4·4

Show that the reaction is of the second order and find the velocity constant for concentrations of 1 mol. per litre. Ans. 14·6.

39. From the electrolysis of hydrochloric acid in a cell with a cadmium anode the following results were obtained: change in concentration of chlorine at anode and cathode respectively ± 0·00545 gram; silver deposited in voltameter connected in series with the cell 0·0986 gram. Calculate the transport numbers of hydrogen and chlorine (Cl = 35·46; Ag = 107·9).

Ans. H = 0·832; Cl = 0·168.

40. The transport number of the cation in potassium chloride was found to be 0·497 and $\lambda_\infty = 130{\cdot}1$.

What is the absolute velocity of K· in cm. per second, under unit potential gradient? Ans. 0·00067 cm./sec.

41. At 18° the velocity of migration of the Ag· ion is 0·00057 cm./sec. and of the NO_3 ion 0·00063 cm./sec. What is the value of μ_∞ for silver nitrate at 18°? Ans. $\mu_\infty = 115{\cdot}8$.

42. Find the degree of ionization of lactic acid at different dilutions and calculate the ionization constant from the following data, valid for 25°:—

v (litres)	64	128	256	512	∞
μv	34·3	47·4	64·2	87·6	381

Ans. 0·000138.

43. If the velocity coefficient for catalysis by N/4 acetic acid is 0·00075, what will be the coefficient when the solution is also N/40 with respect to sodium acetate, assuming that the latter is dissociated to the extent of 86 per cent.? Ans. 0·000075.

44. If an amount of base insufficient for complete saturation is added to an equimolecular mixture of acetate and glycollic acid, in what proportion will the salts be formed? (Dissociation constants at 25°. Acetic acid 0·000018, glycollic acid 0·00015.) Ans. 1 : 2·9.

45. A N/10 solution of sodium acetate is ionized to the extent of 80 per cent. at 18°. What is the osmotic pressure of the solution at this temperature? Ans. 4·28 atmos.

46. Sodium chloride in 0·2 molar solution is dissociated to the extent of 80 per cent. at 18°. What will be the concentration of a urea solution which is isotonic with the salt solution? Ans. 21·6 grams per litre.

47. Calculate the E.M.F. of an oxyhydrogen cell from the facts that



$$2H_2 + O_2 = 2H_2O + 2 \times 68{,}400 \text{ cal.}$$

and that the temperature coefficient of the E.M.F. of the cell is $-0{\cdot}00085$ volts at room temperature (17°). Ans. 1·23 volts.

48. Find the E.M.F. at each electrode and the total E.M.F. of the cell



$$Fe \mid FeSO_4\ 0{\cdot}1N \mid CuSO_4\ 0{\cdot}01\ N \mid Cu$$

at 25°, assuming that the iron salt is 40 per cent. ionized and the copper salt 60 per cent. ionized at the dilutions in question, and that the P.D. at the liquid contact is eliminated. [Use the general formula on p. 388.]

Ans. Fe electrode $- \ 0{\cdot}46 - 0{\cdot}041 = -0{\cdot}501$ volts.
Cu ,, $+0{\cdot}329 - 0{\cdot}064 = +0{\cdot}265$ volts.
Total E.M.F. of cell $- \ 0{\cdot}776$ volts.

49. Discuss the influence of temperature and pressure on the equilibrium



$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 45{,}200 \text{ cal.}$$

and show how the change of the equilibrium constant with temperature can be calculated. (*University Coll., London.*)

50. Criticize the various theories which have been advanced to explain the mechanism of electrolytic conduction.

51. Criticize Berthelot's principle of maximum work.

52. What do you understand by the solubility product? Discuss the question of the simultaneous solubility of two salts possessing a common ion. (*St. Andrews Univ.*)

53. Explain carefully why the ratio of the specific heats of a gas depends on the number of atoms in the molecule.

Briefly describe the method by which for physico-chemical purposes this ratio is determined. (*Sheffield Univ.*)

54. Define the terms "absorption coefficient," "critical solution temperature," "solid solution," and "eutectic alloy," giving examples. (*Sheffield Univ.*)

55. "Every chemical reaction is reversible." Discuss the statement carefully so as to reveal the extent to which it is true, quoting examples. (*Sheffield Univ.*)

56. Write a brief account of the developments in electro-chemistry associated with the names of Daniell, Faraday, Hittorf, and Arrhenius. (*Sheffield Univ.*)

57. How would you determine, either directly or indirectly, the critical temperature, pressure, and volume (or density) of a pure substance? (*Dublin Univ.*)

58. Discuss the conditions on which the possibility of completely separating a mixture of two miscible liquids by fractional distillation depends. (*St. Andrews Univ.*)

59. Discuss the associating and dissociating properties of solvents. (*St. Andrews Univ.*)

60. Describe some experiments in support of the view that ions migrate during electrolysis. How are the transport numbers of ions determined? (*St. Andrews Univ.*)

61. Describe the preparation and properties of some colloidal solutions. What is the present view as to the nature of such solutions? (*St. Andrews Univ.*)

62. Explain why (*a*) a higher potential is necessary to electrolyse a decinormal solution of hydrochloric acid than is necessary for a normal

solution, (*b*) why an E.M.F. is usually set up at the surface of contact of dilute and concentrated solutions of the same electrolyte, (*c*) why magnesium displaces hydrogen slowly from water but rapidly from hydrochloric acid. (*St. Andrews Univ.*)

63. Describe an experiment to illustrate the migration of ions during electrolysis. How would you show that the cation and anion in a solution of copper sulphate move with different velocities, and how would you determine the relative velocities? (*Birmingham Univ.*)

64. State the phase rule and explain the terms involved. Apply the rule to explain the fact that the extent of dissociation of calcium carbonate depends only on the temperature. (*Sheffield Univ.*)

65. What class of substance have in solution molecules of larger size than that calculated from the formula, and how does the phenomenon depend on (*a*) the constitution of the solute, (*b*) the nature of the solvent? (*Sheffield Univ.*)

APPENDIX

EQUIVALENT CONDUCTIVITY AT 18°

Table Ia

Normality of Solution.	KCl.	NaCl.	KNO_3.	$AgNO_3$.	$NaC_2H_3O_2$.	$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2CO_3$.	$\frac{1}{2}BaCl_2$.
0·0000	130·1	109·0	126·5	116·0	78·5	—	—	—
0·0001	129·1	108·1	125·5	115·0	76·8	130·7	—	—
0·0002	128·8	107·8	125·2	114·6	76·4	130·0	—	—
0·0005	128·1	107·2	124·4	113·9	75·8	128·5	—	117·0
0·001	127·3	106·5	123·6	113·2	75·2	126·9	112·0	115·6
0·002	126·3	105·6	122·6	112·1	74·3	—	108·5	—
0·005	124·4	103·8	120·5	110·0	72·4	120·3	102·5	—
0·01	122·4	102·0	118·2	107·8	70·2	115·8	96·2	106·7
0·02	120·0	99·6	115·2	—	67·9	110·4	89·5	102·5
0·05	115·8	95·7	110·0	99·5	64·2	101·9	80·3	96·0
0·1	112·0	92·0	104·8	94·3	61·1	94·9	72·9	90·8
0·2	108·0	87·7	98·7	—	57·1	87·8	65·6	85·2
0·5	102·4	80·9	89·2	77·5	49·4	78·5	54·5	77·3
1	98·3	74·4	80·5	67·6	41·[illegible]	71·6	45·5	70·1
2	92·6	64·8	69·4	—	30·0	—	34·5	60·3

Table Ib

Normality of Solution.	$\frac{1}{2}CuSO_4$.	KOH.	NaOH.	NH_4OH.	HCl.	HNO_3.	$\frac{1}{2}H_2SO_4$.	$HC_2H_3O_2$.
0·0001	110·0	—	—	66	—	—	—	107
0·0002	107·9	—	—	53	—	—	—	80
0·0005	103·5	—	—	38·0	—	—	368	57
0·001	98·5	234	205	28·0	377	375	361	41
0·002	91·9	233	205	20·6	376	374	351	30·2
0·005	81·0	230	204	13·2	373	371	330	20·0
0·01	71·7	228	203	9·6	370	368	308	14·3
0·02	62·4	225	202	7·1	367	364	286	10·4
0·05	51·2	219	199	4·6	360	357	253	6·48
0·1	43·8	217	195	3·3	351	350	225	4·60
0·2	37·7	212	187	2·3	342	340	214	3·24
0·5	—	200	174	1·35	327	324	205	2·01
1	25·8	186	157	0·89	301	310	198	1·32
2	20·1	164	130	0·532	254	258	183	0·80

From Landolt and Börnstein's *Tables*, 1923. Measurements by Kohlrausch and collaborators.

IONIC MOBILITIES (VELOCITIES) IN AQUEOUS SOLUTION AT 18°

TABLE IIa

Normality of Solution.	K.	Na.	Li.	NH_4.	Ag.	½Ba.	½Sr.	½Ca.	½Mg.	½Cu.
0·0000	64·6	43·5	33·4	64·2	54·3	55	51	51	45	46
0·0001	64·1	43·2	33·2	63·6	53·7	54·0	50·4	50·4	44·5	45
0·0002	64·0	43·0	33·0	63·4	53·4	53·5	49·9	49·9	44	44
0·0005	63·7	42·8	32·8	63·0	53·1	52·6	49·0	49·0	43	43
0·001	63·3	42·4	32·5	62·7	52·8	51·4	47·9	48·0	42	42
0·002	62·8	42·0	32·1	62·2	52·2	49·7	46·5	46·6	41	41
0·005	61·8	41·3	31·5	61·2	51·3	46·6	43·9	44·2	39	39
0·01	60·7	40·5	30·8	60·2	50·2	44	41	41·9	37	37
0·02	59·5	39·5	30·0	59·0	49	41	39	39·2	34	34
0·05	57·2	37·9	28·8	56·8	46	—	—	35·2	31	31
0·1	55·1	36·4	27·5	54·8	44	—	—	32·0	28	28

TABLE IIb

Normality of Solution.	H.	Cl.	I.	NO_3.	ClO_3.	$C_2H_3O_2$.	½SO_4.	½C_2O_4.	½CO_3.	OH.
0·0000	315	65·5	66·5	61·7	55·0	35·0	68·3	63	—	174
0·0001	315	64·9	65·6	61·3	54·5	35	66·6	61	—	172
0·0002	314	64·8	65·5	61·1	54·3	34	66·0	60	—	172
0·0005	312	64·4	65·3	60·8	54·0	34	65·0	59	—	171
0·001	311	64·0	64·9	60·4	53·6	33	63·8	58	60	171
0·002	310	63·5	64·4	59·8	53·1	33	—	56	60	170
0·005	309	62·5	63·5	58·8	52·0	32	58·7	54	60	168
0·01	307	61·5	62·7	57·6	50·9	32	55·5	51	55	167
0·02	304	60·2	61·6	56·1	49·3	31	51·5	48	50	165
0·05	301	57·9	60·1	53·3	46·5	30	45	43	43	161
0·1	294	55·8	58·8	50·8	44·0	29	40	39	38	157

From Landolt and Börnstein's *Tables*, 1923. Measurements by Kohlrausch and collaborators.

TRANSPORT NUMBERS OF ANIONS

Table III

n = normality of solution

n =		0 (infinite dilution).	0·01.	0·02.	0·05.	0·1.	0·2.	0·5.	1·0.
KCl, KBr, KI, NH_4Cl	.	0·504	0·504	0·504	0·504	0·504	—	—	0·514
NaCl	.	0·601	0·603	0·603	0·604	0·605	—	—	0·637
LiCl	.	0·663	—	0·672	0·680	0·687	0·690	—	—
KNO_3	.	0·490	—	0·498	—	0·498	—	—	—
$AgNO_3$	.	0·532	—	0·530	—	0·530	0·527	0·519	0·501
$KC_2H_3O_2$	.	0·32	—	—	—	—	—	—	—
KOH	.	0·73	0·73	0·73	0·74	0·74	0·74	—	—
NaOH	.	0·80	0·80	0·80	0·80	0·81	0·82	0·82	0·82
HCl	.	0·172	0·170	—	—	0·162	—	—	0·156
$\frac{1}{2}H_2SO_4$	.	0·180	0·175	0·175	0·170	0·170	0·170	—	—
$\frac{1}{2}BaCl_2$	.	0·54	—	0·56	—	0·58	0·59	—	—
$\frac{1}{2}CaCl_2$	.	0·56	0·57	0·58	0·59	0·60	0·61	—	—
$\frac{1}{2}MgSO_4$	.	0·60	0·61	0·62	0·63	—	—	—	—
$\frac{1}{2}CuSO_4$	.	0·60	—	0·62	0·62	0·63	0·64	—	—

POTENTIAL SERIES OF THE ELEMENTS

Table IV

The numbers in the following table give the potentials of the substances in question in contact with normal ionic solutions of their salts at 25°, referred to three different standards. The numbers under ϵ_{oh} are referred to the potential of the hydrogen electrode as 0·0 volts, those under ϵ_{oc} are referred to the normal calomel electrode as zero, and those under ϵ_c to the calomel electrode = + 0·560 volts.

	ϵ_{oh}.	ϵ_{oc}.	ϵ_c. "Absolute Potentials."
Sodium	−2·7	−2·98	−2·42
Magnesium	−1·55	−1·83	−1·27
Aluminium	−1·34	−1·62	−1·06
Manganese	−1·07	−1·35	−0·79
Zinc	−0·76	−1·04	−0·48
Iron, $Fe/Fe^{\cdot\cdot}$	−0·44	−0·72	−0·16
Cadmium	−0·40	−0·68	−0·12
Thallium	−0·34	−0·62	−0·06
Cobalt	−0·29	−0·57	−0·01
Nickel	−0·22	−0·50	+0·06
Tin, $Sn/Sn^{\cdot\cdot}$	−0·14	−0·42	+0·14
Lead	−0·13	−0·41	+0·15
	+	+	+
Hydrogen	±0·00	−0·283	+0·277
Copper, $Cu/Cu^{\cdot\cdot}$	0·34	0·06	0·62
$Hg/Hg_2^{\cdot\cdot}$	0·80	0·52	1·08
$Hg/Hg^{\cdot\cdot}$	0·86	0·58	1·14
Silver	0·80	0·52	1·08
Platinum	0·86	0·58	1·14
Gold, $Au/Au^{\cdot\cdot\cdot}$	1·3	1·0	1·6
Fluorine	1·9	1·6	2·2
Oxygen[1]	1·2 (1·66)	0·9	1·46
Chlorine	1·40	1·12	1·68
Bromine	1·08	0·80	1·36
Iodine	0·54	0·26	0·82

[1] *Cf.* p. 399. These values apply to a solution of normal $H^{\cdot}$ concentration. In order to liberate oxygen from a solution of normal OH' concentration 0·8 volts less are required, and to liberate hydrogen from the same solution 0·8 volts more are required than in the case of a normal solution of acid.

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